LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
Faculty of Technology
Master's Degree Programme in Energy Technology

Michael Child

INDUSTRIAL-SCALE HYDROTHERMAL CARBONIZATION OF WASTE SLUDGE MATERIALS FOR FUEL PRODUCTION

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Docent Juha Kaikko, D.Sc.
Supervisor: Professor Esa Vakkilainen, D.Sc.

ABSTRACT IN ENGLISH

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Keywords: hydrothermal carbonization, sludge, char, bio-coal, fuel, treatment cost

Hydrothermal carbonization (HTC) is a thermochemical process used in the production of charred matter similar in composition to coal. It involves the use of wet, carbohydrate feedstock, a relatively low temperature environment (180 °C-350 °C) and high autogenous pressure (up to 2.4 MPa) in a closed system. Various applications of the solid char product exist, opening the way for a range of biomass feedstock materials to be exploited that have so far proven to be troublesome due to high water content or other factors. Sludge materials are investigated as candidates for industrial-scale HTC treatment in fuel production. In general, HTC treatment of pulp and paper industry sludge (PPS) and anaerobically digested municipal sewage sludge (ADS) using existing technology is competitive with traditional treatment options, which range in price from EUR 30-80 per ton of wet sludge. PPS and ADS can be treated by HTC for less than EUR 13 and 33, respectively. Opportunities and challenges related to HTC exist, as this relatively new technology moves from laboratory and pilot-scale production to an industrial scale. Feedstock materials, end-products, process conditions and local markets ultimately determine the feasibility of a given HTC operation. However, there is potential for sludge materials to be converted to sustainable bio-coal fuel in a Finnish context.

ABSTRACT IN FINNISH

Lappeenranta University of Technology

Teknillinen tiedekunta

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Michael Child

Industrial-scale hydrothermal carbonization of waste sludge materials for fuel production

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Tarkastajat: Professori TkT Esa Vakkilainen
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Hydrothermal carbonization (HTC) eli märkäpyrolyysi on lämpökemiallinen prosessi, jota käytetään tuottamaan koostumukseltaan hiiltä vastaavaa hiiltynyttä ainetta. Siihen liittyy märkä, hiilihydraattiraaka-aine suhteellisen alhaisissa lämpötiloissa (180 °C – 350 °C) ja korkeassa autogeenisessa paineessa (jopa 2,4 MPa) suljetussa järjestelmässä. Kiinteälle hiilelle on useita mahdollisia käyttökohteita. Tämä avaa mahdollisuuden käyttää useita monia biomassoja, joiden käyttö nykyisin on vaikeaa suuren vesipitoisuuden tai muun syyn vuoksi. Lietemateriaaleja tutkitaan mahdollisina raaka-aineina kiinteän polttoaineen tuottamiseksi teollisen mittakaavan HTC- prosessilla. Yleensä sellu- ja paperiteollisuuden lietteen (PPS) ja anaerobisesti pilkotun kuntien puhdistamolieteen (ADS) käsittely nykyisellä HTC-tekniikalla on kilpailukykyistä perinteisten käsittelyvaihtoehtojen kanssa, jonka hinta vaihtelee alkaen 30–80 €/t märkää lietettä. Vastaavasti lietteet voidaan käsitellä HTC prosessissa alle 13 €/t (PPS) ja 33 €/t (ADS). HTC-prosessiin liittyy mahdollisuuksia ja haasteita, koska tekniikka on suhteellisen uusi, ja vasta siirtymässä laboratorio- ja pilotti-mittakaavan tuotannosta teolliseen mittakaavaan. Syöteaineet, lopputuotteet, prosessin olosuhteet ja paikalliset markkinat viime kädessä määräävät, onko tietty HTC-toiminta mahdollista. On kuitenkin mahdollista, että lietteen materiaaleja voidaan muuntaa kestäväksi bio-hiili polttoaineeksi Suomen oloissa.

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There are very few worthwhile things in life that can be accomplished alone. So, while I remain very pleased with the work completed, I must acknowledge a number of people and institutions that helped me achieve what I set out to, and inspired me to reach well beyond what I thought was my potential. I am greatly indebted to all of them. First, I would like to express my thanks to my supervisor, Professor Esa Vakkilainen, for his help and guidance throughout this entire process and to Docent Juha Kaikko for reviewing the original text. It was also an honour to be part of the *Biomassan märkäpyrolyysin uudet sovellukset* project and to work for such fine corporate partners as UPM, Ekokem, Teollisuuden vesi and Akvafilter. Second, I would like to thank the classmates that I had the opportunity to work with throughout my Master's studies at LUT. An atmosphere of co-operation and respect for others was established from the very beginning of our studies. Sometimes I led, sometimes I followed. Each time it was a pleasure and privilege to learn in such a diverse and multi-cultural environment. In the end, we accomplished much more together than we could have on our own. Lastly, I would like to thank my greatest partners in life, Lucas, Heili and Christel Child, who I never once lost sight of during my studies. They each made sacrifices to allow me the opportunity to return to study at LUT. They each share in this accomplishment. Only one author's name appears on the cover, but a family did this work.

Michael Child

June 3, 2014

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LIST OF SYMBOLS, ABBREVIATIONS AND DEFINITIONS

Activated carbon	a char subjected to reaction with gases and possibly chemicals during or after carbonization in order to create improved absorptive properties
Activated charcoal	popularly used interchangeably with activated carbon
ADS	anaerobically digested municipal sewage sludge
AR	as received
Biochar	char used as a soil additive for a specific purpose
Bio-coal	popular terms used interchangeably with char, especially a finished product
°C	degrees Celsius
Char	solid decomposition product of a natural or synthetic organic material
Charcoal	char obtained from organic material and used for cooking
CHP	combined heat and power
COD	chemical oxygen demand
Coke	solid product of pyrolysis or organic material which has passed, at least in part, through a liquid or liquid-crystalline state during carbonization
DAF	dry ash free
DB	dry basis
DM	dry matter
EU	European Union
EUR	Euro
HTC char	the char product of hydrothermal carbonization

HHV	higher heating value
HTC	hydrothermal carbonization
kJ	kilojoule
kWh_e	kilowatt hour of electricity
kWh_th	kilowatt hour of thermal energy (steam)
LHV	lower heating value
MJ	megajoule
mm	micrometre
MPa	megapascal
MWh	megawatt hour
PPS	pulp and paper industry sludge
SEM	scanning electron microscope
SNG	synthetic natural gas
TOC	total organic carbon
TS	total solids
TWh	terawatt hour

1 INTRODUCTION

1.1 General introduction

In the world of martial arts, one of the most effective techniques for neutralizing an opponent is to use their own momentum against them rather than directly opposing it. The word *Judo* itself means ‘the gentle way’ and is embodied by the concept of *jū yoku gō o seisu*, or ‘gentleness controls hardness’. Main principles of Judo include *seiryoku zen'yō,* ‘maximum efficiency, minimum effort’ and *jita kyōei*, ‘mutual welfare and benefit’. Perhaps one of the most popularly recognizable categories of Judo is *nage waza*, or ‘throwing techniques’. Moreover, in order to successfully throw an opponent, a defender must create an initial imbalance, turn in and ‘fit’ into a throw, and then execute the throw itself (Matsumoto, 1996; Yoffie & Kwak, 2002).

Global carbon dioxide levels are estimated to be hovering around the symbolic 400 ppm level (Shukman, 2013) and most certainly increasing as a result of human activities (Intergovernmental Panel on Climate Change, 2013). From this it could be concluded that an environmental imbalance exists. Reports of current effects and future results of global warming can be viewed as warnings that the planet may have something particularly dire in store for humanity. At the same time, efforts to combat the carbon problem are seen globally at individual, societal, industrial, institutional, governmental and intergovernmental levels. At this point it is just unclear which side will be thrown, which will do the throwing and when the throwing will actually occur. In such struggles between organisms and the planet historically, the planet has always won and carbon is usually involved one way or another. Whether the cause has been volcanic activity, changes in ocean currents or meteor impacts, the planet has responded several times with significant changes in global temperatures. Perhaps dramatic global change in the carbon cycle is ‘the throw’. However, some struggles have lasted longer and been more ‘successful’ than others. Our own is just beginning. Reactions on how we are doing appear to be mixed.

Perhaps the greatest feature of modern *Homo sapiens* is our ability to be sapient. This wisdom has enabled us to analyse, regulate and adapt to the social, economic and environmental conditions around us. This wisdom has also allowed us to inflict damage on ourselves and the environment to concerning levels. It is inevitable that the planet will have the final throw, but we do not need to make it so easy. Perhaps we can get in a few throws of our own before the struggle is over.

There are signs that humanity is developing a ‘gentle way’ of dealing with the carbon problem. The concepts of Green Chemistry and Sustainable Development could be seen, at least partly, as embodiments of the principles of ‘maximum efficiency, minimum effort’ as well as ‘mutual welfare and benefit’, respectively. The search is on to develop products and processes that not only add value, but are socially, economically and environmentally sustainable. Currently, there are enormous efforts to find or develop affordable, renewable forms of raw materials and energy, reduce or eliminate waste of all forms, and effectively manage waste that is inevitably generated.

Growing research into the process of hydrothermal carbonization (HTC) may offer an opportunity to better ‘fit’ into a throw of our own. Instead of merely opposing all things carbon, knowledge of the very nature, shape and structural properties of carbon materials can be used to neutralize or even negate certain harmful effects (Hu *et al.*, 2010; Titirici *et al.*, 2007). At the same time, HTC may offer novel applications for sustainable, value-added products.

1.2 Objective of the thesis

The objective of this thesis is to explore the general feasibility of industrial-scale hydrothermal carbonization treatment, using existing technology, of two biomass waste streams: pulp and paper industry sludge, and anaerobically digested sewage sludge. Four scenarios will be proposed for the treatment of these sludge materials and the ultimate costs of treatment will be calculated and compared for each waste stream. It will not be the intention of this thesis to compare the relative strengths of the feedstock materials themselves or the technologies used to derive the HTC products. After commenting on general feasibility of HTC treatment, more specific opportunities and challenges related to social, environmental and economic factors will be discussed. Final conclusions will be preceded by a list of recommendations for parties considering the viability of HTC processing of these sludge materials in a given context.

1.3 Structure of the thesis

After this introductory section, Section 2 of this thesis will explore the theoretical background of hydrothermal carbonization, from its beginnings to modern best available technology. Throughout this section feedstock materials, HTC process conditions, and end products will be discussed. Section 3 will introduce the aims of the current study as well as detail aspects of the four scenarios under investigation. Section 4 will then examine issues related to flows of material and energy. This will be followed by an economic analysis of each scenario in Section 5. Sections 6 through 8 will discuss both opportunities and challenges related to the HTC process in terms of social, environmental and economic sustainability. Section 9 will review some specific recommendations related to HTC plant design and make conclusions on the ultimate feasibility of industrial-scale HTC operations.

2 BACKGROUND

2.1 Historical development of hydrothermal carbonization

In 1913, Friedrich Bergius outlined not only a way of transforming coal into a liquid fuel, but of transforming carbohydrates into a coal-like material. Eventually, Bergius would be awarded the Nobel Prize in Chemistry in 1931 (along with Carl Bosch) "in recognition of their contributions to the invention and development of chemical high pressure methods" (Kauffman, 1990). Some of these contributions, however, would remain mostly academic as abundances of cheap, real coal made the use of a coal-like substance quite unnecessary. Indeed, Bergius appears not to have been so interested in the coal-like end product, but was busy converting both it and real coal into liquid or gaseous hydrocarbon fuel (Bergius, 1966). Lack of interest in coal may have resulted from a view that liquid and gaseous fuels were superior energy carriers (Funke & Ziegler, 2010). Fortunately, scientific interest remained high enough in subsequent years that work on ‘new forms of carbon’ and their possible applications would continue (Wang *et al.*, 2001). By the turn of the twenty-first century, the world at large may have experience a “renaissance” in the synthesis of carbonaceous materials to the extent that some researchers claim we are currently “back in the black” (Titirici *et al*., 2007).

Hydrothermal carbonization is a thermochemical process used in the production of charred matter similar in composition to coal. In general, it involves the use of wet, carbohydrate feedstock, a relatively low temperature environment (180°C-350°C) and high autogenous pressure (up to 2.4 MPa) in a closed system. Typically, biomass or a source of starch is converted into a valuable carbon material in the form of a solid char. Other products include non-condensable gases (mostly CO_2), aqueous phase products (residues, sugars and organic acids) and water (Hoekman *et al*., 2011). In recent years, interest in the potential applications of various carbon materials has been high. At this point, possibilities for HTC end products include mechanisms of drug delivery, catalysts, adsorbents, soil enrichers, energy storage systems, fuel cell components, and sources of fuel (Titirici & Antonietti, 2010). As the mechanisms of HTC reactions become better understood and as the number of successful feedstock materials increases, the potential for further exploitation of an increasing range of carbon materials appears great.

2.2 Carbonization and char production

Under normal conditions, terrestrial and aquatic biomasses sequester atmospheric CO_2 through respiration and photosynthesis. Eventually, plants die and are then digested or degraded by organisms that eventually pass the organic material back into the atmosphere, generally in the form of a CO_2-equivalent gas. In some cases, organic material can collect in solid sediments that eventually form, for example, peat-like deposits. Under the pressure of further deposition and the absence of oxygen, and over very long periods of time, these deposits may be converted into gas, oil or coal through dissociation reactions, thereby creating a carbon sink (Hu *et al*., 2010; Libra *et al*., 2011; Titirici *et al*., 2007; Titirici & Antonietti, 2010). Indeed, what makes them such non-renewable resources is the time they take to form - millions of years in the case of lignite (Titirici & Antonietti, 2010). A main issue in the global carbon problem is that human activity has excessively been transferring the carbon from sinks to the atmosphere at an alarming and increasing rate. Therefore, the idea of speeding up the process of carbonization in order to replete the sinks has great appeal.

The thermochemical production of a char, or coal-like substance, can also be achieved over relatively short periods of time. Five such mechanisms are described in the following sections. Each falls under a general characterization of pyrolysis, yet each differ in process conditions as well as the properties and amounts of solid, liquid and gaseous end products. It should be noted that this list of mechanisms is not exhaustive. Figure 1 provides a general characterization of industrial char production. Table 1 shows a general overview of how conditions typically vary within these same processes. Values expressed are supported by literature, but some represent generalizations of highly variable conditions. Appropriate caution should be exercised when interpreting values as the intention is to provide an overview of how variables influence product yield distribution.

Libra *et al.* (2011) noted a need for clarification and standardization of certain terms referring to the solid products of both dry and wet pyrolysis. This text will generally follow the same consistent usage of terms. Char is “a solid decomposition product of a natural or synthetic organic material" (Fitzer *et al.*, 1995). This general scientific usage of the term char will be followed in this text although the more popular term bio-coal will also be used to refer generally to any char material, especially one that is offered as a finished product. When variants are needed, the word char will be preceded by a specific process term (e.g. pyrolysis char, HTC char, etc.). HTC char will refer to the char product of hydrothermal carbonization. Although the word hydrochar is commonly used for the same material (*ibid*.), this term will not be used subsequently in this text. Activated carbon is "a char which has been subjected to reaction with gases, sometimes with the addition of chemicals … during or after carbonization in order to increase its adsorptive properties" (*ibid*.). The term activated charcoal is commonly used to refer to the same material but will not be used subsequently in this text. Charcoal is "a traditional term for a char obtained from wood, peat, coal or some related organic materials" (*ibid*.). In this text charcoal will refer only to char material which is usually reserved for cooking (Libra *et al*., 2011). Coke is "produced by pyrolysis or organic material which has passed, at least in part, through a liquid or liquid-crystalline state during the carbonization process" (Fitzer *et al*., 1995). Biochar will refer strictly to char used as a soil additive for a specific purpose (Libra *et al*., 2011).

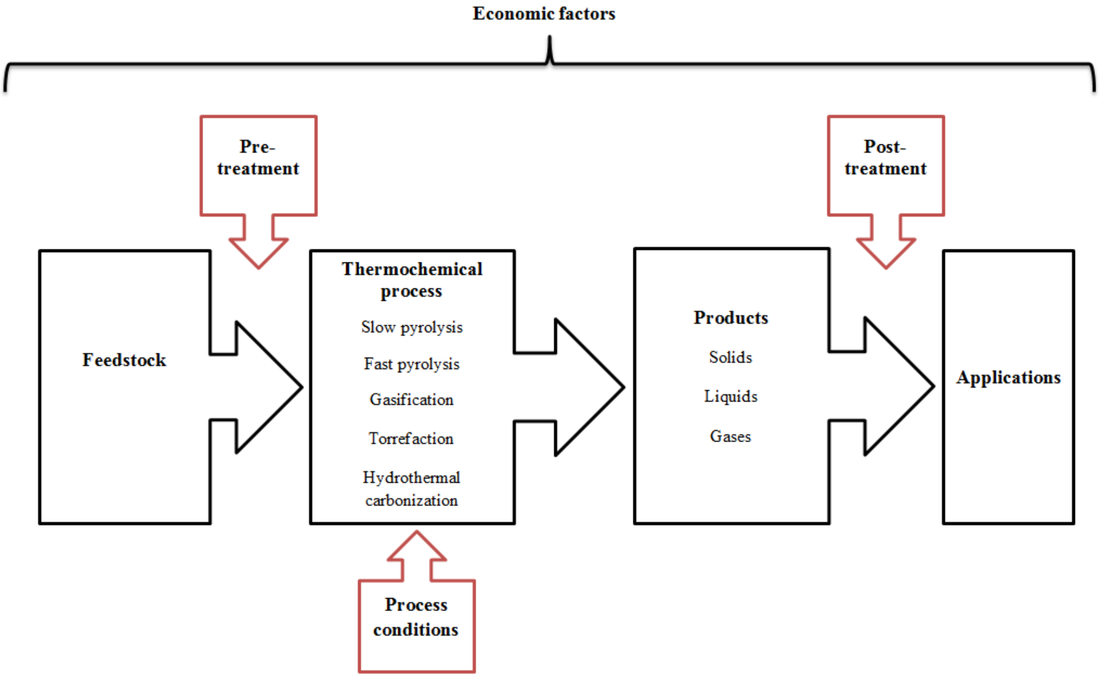


Figure 1: Factors influencing the production and application of char (Adapted from Libra *et al*., 2011)

2.2.1 Conventional pyrolysis

Slow pyrolysis is a process that has been traditionally used for thousands of years to produce charcoal. As the name suggests, the organic material is heated over relatively long periods of time at temperatures of around 400°C. The main yield is solid char, although tar-like substances and gases are also produced (Demirbas & Arin, 2002). Reaction temperatures and residence times can be adjusted in order to promote a desired product yield. In general, lower temperatures and longer residence times will yield higher amounts of solid products. As temperatures rise and residence times decrease, higher yields of gaseous and liquid products are achieved. For this reason, some authors choose to distinguish between slow and intermediate pyrolysis (Libra *et al*., 2011).

2.2.2 Fast pyrolysis

Fast pyrolysis involves the rapid heating (500°C - 1000°C) and devolatilization of organic fuels by thermochemical processes in the presence of little or no oxygen. Products of the process are primarily small amounts of char and relatively large amounts of vapour which contain tars and volatile gases that are rapidly quenched into a liquid form. These liquids can then be further refined as useful fuels. While the char itself may have several uses (that will be discussed in subsequent sections), the focus of fast pyrolysis is generally on the yield of liquid products (up to 75%) (Libra *et al*., 2011). At very high temperatures and very low residence times, one can distinguish fast pyrolysis from flash pyrolysis (Demirbas & Arin, 2002).

2.2.3 Gasification

Gasification is similar to pyrolysis in that it involves the heating and devolatilization of organic fuels. In this case, enough oxygen is present so that partial combustion may occur. Temperatures remain high (approximately 800°C) throughout the process in order to encourage high yields (up to 85%) of gaseous products, or syngas, which are typically used directly. Alternatively, they can be purified and used as gaseous fuels such as synthetic natural gas (SNG) or in subsequent production of liquid fuels. As temperatures are generally higher than during pyrolysis and residence times are generally short (~10-20 seconds), gasification yields very little char (10%) and even less liquid product (5%) (Libra *et al*., 2011).

2.2.4 Torrefaction

Torrefaction is also known as mild pyrolysis that occurs at relatively low temperatures (200-300°C) over moderate residence times (1-3 hours). Importantly, the torrefaction process begins with stages of initial heating, pre-drying, post-drying and intermediate heating designed to facilitate evaporation of water and attain a target torrefaction temperature. These stages may involve the consumption of external energy or auto-consumption of gaseous products to generate heat. Although torrefaction plants are generally located close to a source of waste or superfluous heat, added expense or diminished efficiency may result when this kind of heat is not available. Main products of torrefaction are fairly high levels of char (70%) and torrefaction gas (30%). Torrefaction gas contains large yields of products that can be condensed into liquids. These gaseous or liquid products are often used to provide heat for the torrefaction process, but can also be cleaned (as they will contain tars), collected and used elsewhere (Van der Stelt *et al.*, 2011). Solid products of torrefaction are currently being used as combustion, gasification and fast pyrolysis fuels, often as a replacement for coal or in co-firing (*ibid.*). In general, torrefaction can yield char that has an improved mass and energy balance over the original feedstock, resulting in improved heating values. In addition, torrefaction char has improved grindability, resulting in less energy use for size reduction before firing. Lastly, torrefaction char has lower equilibrium moisture content and, therefore, higher density. This results in lower transport and storage costs as well as higher received heating values. However, recent discussion suggests that key properties and benefits are rarely achieved at the same time, and that economically profitable large-scale production should not be assumed (Agar & Wihersaari, 2012).

2.2.5 Hydrothermal carbonization

Hydrothermal carbonization involves the use of wet, carbohydrate feedstock, a relatively low temperature environment (180°C-350°C) and high autogenous pressure (up to 2.4 MPa) in a closed system. Typically, biomass is converted into a valuable carbon material in the form of a char. Other products include non-condensable gases (mostly CO_2), aqueous phase products (residues, sugars and organic acids) and water (Hoekman *et al.*, 2011). More detailed information about this process will follow in subsequent sections.

2.2.6 Interaction of system variables

The purpose of the discussion so far is to show how a myriad of factors interact within different systems which ultimately can lead to the production of char and other materials that have some kind of application. Clear from this discussion is that Figure 1 can be viewed in a bi-directional manner. For example, if one desired a particular primary outcome, say the production of a liquid fuel, multiple pathways could be traced back to a variety of possible feedstock materials. The one deemed most optimal would depend on a number of factors including how exactly the product would be derived and from what kind of feedstock. Economic determinants would include feedstock issues such as price, availability and transport costs; production issues such as plant size and capacity, investment costs, labour, automatization and maintenance; and product issues such as quality, end-of-life treatment and market competition (Libra *et al*., 2011). Alternatively, one could begin from a particular feedstock, perhaps one that is cheap, renewable and readily available, and then explore the pathways that can lead to a number of economically viable applications. Ultimately, it was the goal of this section to examine different systems holistically. In subsequent sections some of the layers will be peeled back in order to look a particular system from both directions.

Table 1: Comparison of thermochemical treatments and typical product yields

Process	Process conditions						Approximate product yield (weight%)		
	Temperature range (°C)	**Heating rate**	**Residence time**	**Pressure**	**Surrounding medium**	**Cooling rate**	**Char**	**Liquid**	**Gas**
Slow pyrolysis	~400	Slow[b]	Hours to weeks	Low[c]	Little or no O_2	Slow	35	30	35
Fast pyrolysis	~500	Fast[b]	Seconds	Variable[c]	Little or no O_2	Rapid	12	75	13
Gasification	>800[a]	Fast[c]	10-20s	Variable[c]	Lightly reducing atmosphere	-	<10	5	>85
Torrefaction	200-300[a]	Moderate[a]	Several hours[a]	Atmospheric[a]	Little or no O_2[a]	None[a]	70[a]	0[a]	30[a]
Hydrothermal carbonization	180-350	Moderate	No vapour residence time; processing time from minutes to several hours	High Autogenous	Water	Slow	50-80	5-20	2-5

All values are approximations provided by Libra *et al*. (2011) unless denoted otherwise.
a (Van der Stelt *et al*., 2011)
b (Demirbas & Arin, 2002)
c Values are highly variable and depend on desired distribution of product yield. Values expressed are generalizations by the author.

2.3 Hydrothermal synthesis of carbon materials

In many dry thermochemical processes, such as pyrolysis or combustion, moisture levels associated with many types of renewable resources are often seen as troublesome. Liquid water ‘gets in the way’ of reactions and efforts are usually made to dry reactants ahead of time. This may require energy that can be expensive or detract from process efficiency (i.e., some of the energy created must be used in the drying process, thereby reducing overall conversion efficiency) when a source of waste or superfluous heat is unavailable. Another approach is to utilize a wet thermochemical process, such as HTC, in order to take advantage of the fact that water can be “an excellent reaction environment, reactant and solvent for a diverse range of reactions” (Kruse *et al.*, 2013). One obvious advantage of HTC is that a wider range of potential feedstock materials can be exploited, such as biomass and waste, which have relatively high water content. Another advantage is that carbon materials, which have traditionally been derived from fossil resources, such as peat or coal, can now be derived from renewable resources. Interestingly, careful manipulation of reactants, process conditions or post-treatment can result in highly functionalized carbon material production by HTC from a wide variety of feedstock materials. Recent reviews have gone as far as to state that HTC chemistry “offers huge potential to influence product characteristics on demand, and produce designer carbon materials” (Libra *et al*., 2011). A further advantage of utilizing waste streams is that much of the cost of and need for waste treatment can be avoided as substances that are traditionally viewed as waste can be converted directly into value-added material (*ibid*.). A final advantage that has created a great deal of current interest is how HTC products cannot only be viewed as carbon-neutral, but can also be utilized as a way of reducing carbon dioxide produced from past industrial activities (Titirici *et al*., 2007).

2.3.1 Carbohydrates

A simplified model of how carbon can be exploited from carbohydrates has been proposed by researchers (Titirici *et al*., 2007) based on the stored combustion energy and the ‘carbon efficiency’ of the transformation. Table 2 shows some common conversion processes for glucose in such a manner. Accordingly, transformation of glucose into carbon material during HTC results in no theoretical yield of CO, CO_2, CH_4 or H_2. Of course, some yield of such products in real life can be expected as more complex carbohydrates and proteins are found in typical feedstock materials such as biomass and waste. Still, the efficiency with which carbon is retained within the desired products is remarkably high for HTC.

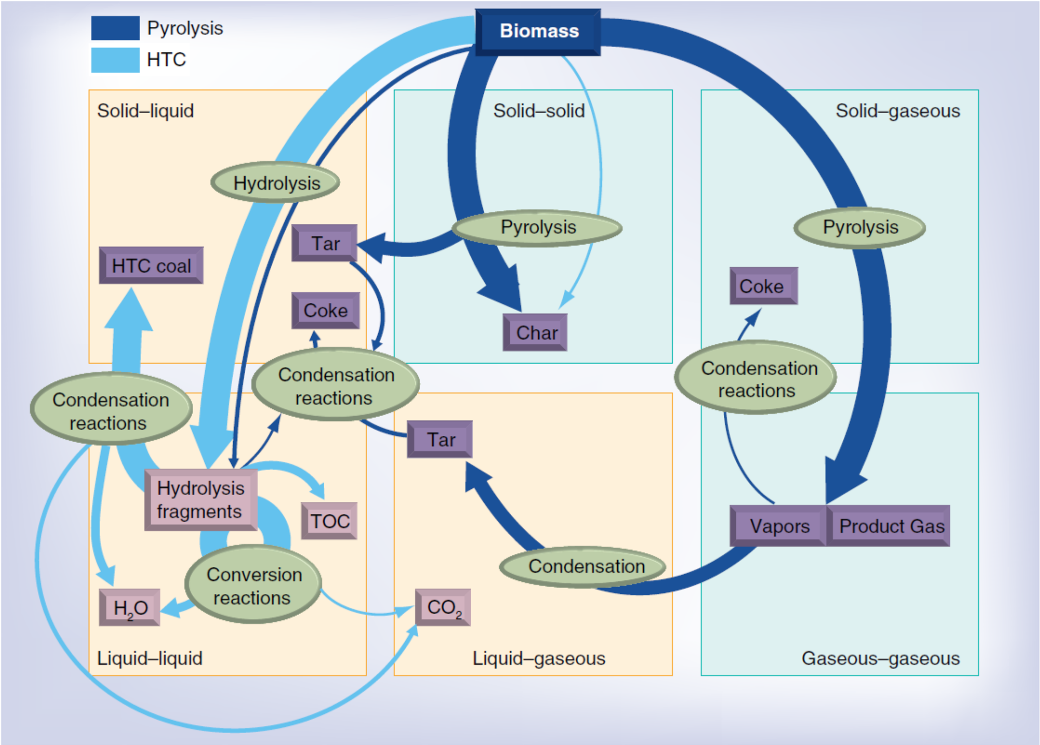
Table 2: Comparison of common carbon conversion pathways

	Process	**Products**	**Carbon efficiency (%)**	**Stored combustion energy (kJ)**
Carbohydrate ($C_6H_{12}O_6$)	Combustion	$6CO_2 + 6H_2O$	0	0
	Fermentation	$2C_2H_5OH + 2CO_2$	66	2760
	Anaerobic digestion	$3CO_2 + 3CH_4$	50	2664
	Hydrothermal carbonization	$C_6H_4O_2 + 4H_2O$	100	2200

2.3.2 Biomass

The conversion of biomass into carbon materials by HTC is quite complex and follows several parallel pathways, only some of which are fully understood in terms of when and how they occur (Funke & Ziegler, 2010). In general, the mechanisms involved in HTC are hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization (see Figures 2 and 3). While many of these mechanisms involve several reactions that can occur in parallel, the HTC process primarily begins with the hydrolysis of carbohydrate material. Hydrolysis of hemi-cellulose will begin at approximately 180°C, while hydrolysis of cellulose and lignin will begin to occur above 200°C. Complete hydrolysis of both lignin and cellulose is not likely to occur, leading many to conclude that two reaction pathways lead to solid formation, one in a liquid state and the other in a solid state *(*He *et al., 2013;* Kruse *et al.*, 2013). Reactants in the liquid state will then undergo dehydration or decarboxylation. These mechanisms are particularly important as oxygen and hydrogen are removed, leading to char with lower O/C and H/C ratios than the original feedstock. Accordingly, heating values of HTC char are reported to approach that of lignite and brown coal (Hoekman *et al.*, 2011; Libra *et al.*, 2011; Sevilla & Fuertes, 2009; Xiao *et al.*, 2012). Fragments of hydrolysis, decarboxylation and dehydration reactions can also undergo condensation, polymerization or aromatization although it is so far unclear exactly how this happens (Funke & Ziegler, 2010; Kruse *et al.*, 2013). The resulting precipitates can form the majority of the liquid product of HTC and are often seen as undesirable end products under the name of Total Organic Carbon (TOC) (Libra *et al*., 2011; Yan *et al*., 2010). Other mechanisms postulated to be involved in HTC to at least a small degree are demethylation, demethanation, transformation reactions, pyrolysis and Fischer-Tropsch-type reactions (Funke & Ziegler, 2010; Xiao *et al*., 2012). These mechanisms are speculated upon based on relatively small amounts of HTC end products.

Figure 2 shows a simplified reaction scheme comparison for both HTC and dry pyrolysis. Figure 3 shows the scheme for HTC in more detail. More thorough discussion can be found from the literature (Funke & Ziegler, 2010; Kruse *et al*., 2013; Libra *et al*., 2011; Sevilla & Fuertes, 2009) and will be presented in subsequent sections as needed.



TOC – Total Organic Carbon in the form of organic acids, furfurals and phenols among others

Figure 2: Simplified reaction schemes of HTC and dry pyrolysis (Libra *et al*., 2011)

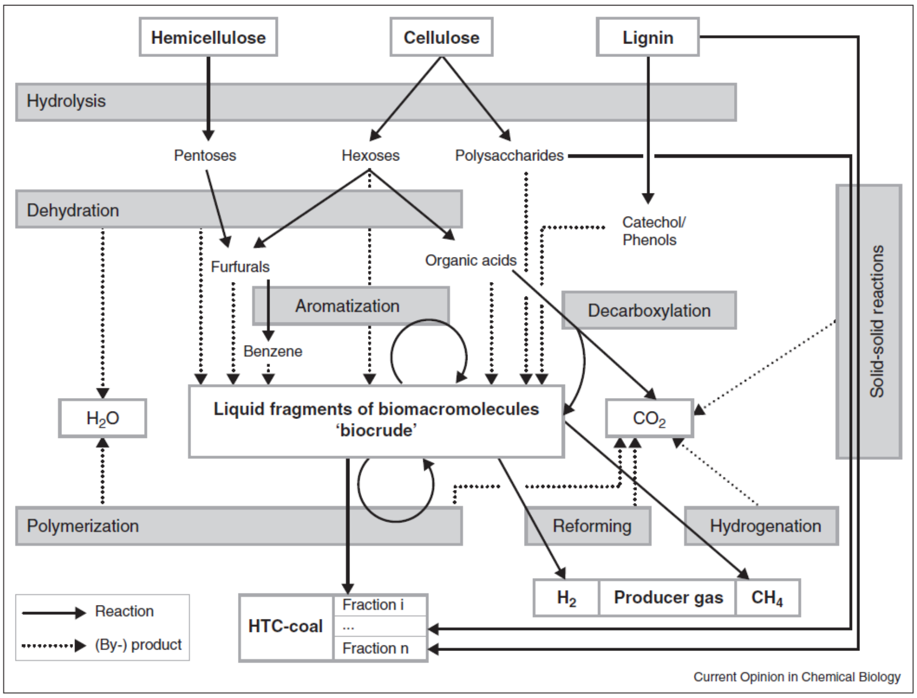


Figure 3: Detailed reaction scheme of HTC (Kruse *et al*., 2013)

2.3.3 Waste

Most of the waste streams used for HTC research consisted of those high in biomass. For this reason, chemical pathways are the same as those previously discussed. However, a number of researchers have expanded the range of feedstock materials tested to include those which contain significant amounts of protein, such as sewage sludge and certain types of food waste (He *et al*., 2013; Ramke *et al*., 2009). Figure 4 shows a typical reaction scheme for sewage sludge. Importantly, the presence of protein in some feedstock materials does not appear to have a significant effect on product outcomes. There is some concern, however, that levels of coalification of food waste and sewage sludge are not "fully reached" as H/C ratios of chars from these streams are relatively higher (Ramke *et al*., 2009). Of greater concern are the potential effects of glass and metal in some waste streams, such as mixed municipal solid waste. These components will not be affected by HTC and therefore may skew results to make it appear that solid yields of char are greater than they actually are (Berge *et al*., 2011). In addition, metals such as silver and iron oxides may have variable catalytic effects during HTC. However, no noticeable effects have thus far been associated with metal components of mixed MSW as the major component is aluminium, which is not thought to influence solid yield (*ibid*.).

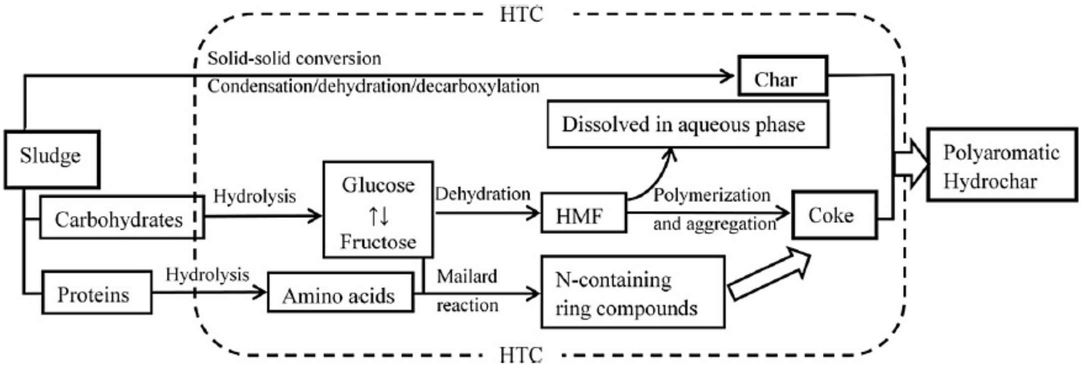


Figure 4: Reaction scheme of sewage sludge (He et al., 2013)

Interestingly, a claim was made by Lu *et al.* (2012) that an advantage of the HTC of solid waste is that "emerging compounds, such as pharmaceuticals, personal care products, and endocrine disrupting compounds, which currently pose significant environmental concerns in landfills… may be thermally degraded or transformed during carbonization". The authors cite Berge *et al.* (2011), who make the exact claim while citing Libra *et al.* (2011) as a source. The statement referred to in that article may be that "high process temperatures can destroy pathogens and potentially organic contaminants such as pharmaceutically active compounds" (*ibid*.). However, Libra *et al.* (2011) cite two articles as the source of this information that involves only a single waste stream (sewage sludge). In addition, neither investigation involved HTC at all nor did they utilize thermochemical processes that operated in temperature ranges typically associated with HTC (Bridle *et al.*, 1990; Sütterlin *et al.*, 2007). It remains unproven whether HTC has the capacity to remove such compounds.

2.4 Process conditions of hydrothermal carbonization

Funke and Ziegler (2010) outline a number of general operational conditions that are associated with HTC while cautioning that a strict, common definition has yet to be established. Firstly, subcritical conditions of water must exist in order to impede hydrothermal gasification that would result in gaseous carbon products such as CH_4 and H_2. Second, temperatures must exceed 100°C in order for reactions to begin. However, it has been noticed that practical implementation of HTC is unlikely outside the range of 180-250°C. Third, liquid water must be present; therefore, at least saturated pressure is necessary. Fourth, feedstock needs to be completely submerged throughout the process. In the absence of contact with water, biomacromolecules may undergo pyrolytic reactions that create such products as CO and tars. In real life situations, this is likely to occur to a small degree and may help to explain the production of trace amounts of these substances during HTC. In addition, reactant material above the liquid surface may not carbonize. Fifth, a neutral or weakly acidic environment will improve the rate of reactions in HTC. Sixth, residence times will typically vary between 1 and 72 hours. Together with the temperature regime, residence times combine to produce a ‘reaction severity’. Higher temperatures or longer residence times represent a high reaction severity. In such conditions, lower yields of solid product are found, yet these products tend to have higher carbon content (Funke & Ziegler, 2010).

2.4.1 Process considerations

It has been noted that process mechanisms and the effects of process conditions depend highly on the nature of the feedstock (Funke & Ziegler, 2010). For this reason, optimal overall process design will be unique for each type of feed. At the same time, some generalizations can be made in this regard. First, a high biomass to water ratio will result in better polymerization and higher overall solid product yields (Stemann *et al.*, 2013). Less water usage may also result in lower energetic and investment costs. This may also make wet feedstock particularly attractive. Second, longer residence times can ensure more complete reactions and result in less loss of organic material in the wastewater. For both these reasons, at least partial recirculation of water can be considered. Third, higher temperatures will generally speed up HTC and result in higher carbon content of solid products, but higher pressures will be experienced. This may result in higher investment and energy costs. Finally, pre-treatment of biomass or waste feedstock in the form of grinding may be of some advantage in order to control and speed up the rate-determining step of hydrolysis. Again, energy demands and investment costs may be associated with such pre-treatment (Funke & Ziegler, 2010; Hoekman *et al.*, 2011).

2.5 Products of hydrothermal carbonization

Table 1 shows the approximate yield distribution for solid, liquid and gaseous products of HTC. It should be reiterated that this distribution was provided as a representative overview. Yield distributions depend heavily on both feedstock and process conditions (Funke & Ziegler, 2010). As these are inherently variable, so are reported results. Table 3 shows reported results from various sources. As can be seen, analyses concentrate heavily on measurements of solid products and often do not include values for liquid or gaseous products. Mass balances for HTC are not currently available as those so far reported are either incomplete or apply to carbon only (*ibid*.). Despite this shortcoming, generalizations can be made concerning the characteristics of the products.

Table 3: Reported product distribution yields of HTC

Product yield (%)			**Feedstock**	**Source**
Solid	**Liquid**	**Gas**		
50-80	5-20	2-5	Biomass, waste materials	(Libra *et al*., 2011; Lu *et al*., 2012)
20-50	-	-	Municipal Solid Waste, Paper, Food waste	(Lu et al., 2012)
75-80	15-20	5	Variety of organic waste materials	(Ramke et al., 2009)
36-66	-	-	Cellulose, peat, wood	(Funke & Ziegler, 2010)
30-50	-	-	Cellulose	(Sevilla & Fuertes, 2009)
50-69	12-14	5-12	Jeffery Pine and White Fir mix	(Hoekman et al., 2011)
35-38	-	-	Corn stalk, forest waste	(Xiao et al., 2012)
63-83	8-17	9-20	Loblolly Pine	(Yan et al., 2010)

2.5.1 Gaseous products

As can be seen from Table 3, reported gas yields have varied significantly for HTC, and have done so even under identical experimental conditions (Funke & Ziegler, 2010). CO_2 is the main gaseous product, although CO, CH_4, H_2 and other gaseous hydrocarbons are also found. In general, rising reaction temperatures lead to increases in gaseous yield. As stated previously, decarboxylation is an important mechanism of HTC that can help explain the presence of CO_2. It is also known that decarboxylation is temperature sensitive and will increase as process temperatures increase. This is of particular important due to the fact that decarboxylation is responsible for the removal of oxygen from the feedstock. The result is that solid products will have a lower O/C ratio and, thereby, a higher heating value. Moreover, it has been reported that as gaseous yields increase, higher yields of both CH_4 and H_2 are seen. At the same time, lower yields of CO are reported. This may also result in slightly higher heating values as H/C ratios of solid products decrease accordingly. Funke and Ziegler (*ibid.*) suggest that measurement of gaseous products, particularly CO_2, may provide a potential process control parameter that gives useful information regarding reaction progress. At this time, there is no mention in the literature of possible capture and usage of product gases although this remains a possible area of development as the scale of HTC operations increases.

2.5.2 Liquid products

Water has multiple roles in HTC as a medium of heat transfer, solvent, reactant and product (Funke & Ziegler, 2010). During hydrolysis, large amounts of water are consumed in the degradation of carbohydrates and proteins, but this is followed by large amounts of liquid water formation during subsequent dehydration reactions, also referred to as dewatering. As process temperature increases, so does overall water formation (Hoekman *et al.*, 2011; Yan *et al.*, 2010). However, at temperatures of 200°C, a small net loss of water was noticed (Yan *et al.*, 2010).

The involvement of water in HTC results in relatively significant loads of various organic and inorganic compounds present in the liquid phase. In general, these compounds have been regarded as undesired side-products, comprised mostly of organic acids, sugars and the derivatives of both sugars and lignin (Funke & Ziegler, 2010; Hoekman *et al.*, 2011; Ramke *et al.*, 2009; Xiao *et al.*, 2012; Yan *et al.*, 2010). Xiao *et al.* (2012) offer an exhaustive list of the compounds found in liquid HTC products (presented and discussed subsequently as Table 20). The amount of these materials, often denoted as Total Organic Carbon (TOC), is seen to decrease as reaction severity increases (Hoekman *et al.*, 2011). Despite the significant levels of TOC in the HTC liquid product, researchers report that the wastewater of HTC can be effectively treated by typical aerobic and anaerobic means (Funke & Ziegler, 2010; Ramke *et al.*, 2009).

Funke and Ziegler (2010) advise that many organic compounds can be found in significant quantities in the HTC liquid product and should be seen as valuable materials. Failing to do so may represent a potential loss if they are not recovered. Xiao *et al.* (2012) suggest that these compounds might be suitable for biodiesel or chemical production. Ramke (2009) claims that methane capture could result from anaerobic degradation of the organic products found in the liquid phase. Also, partial recirculation of process liquid products is a possible benefit as the liquid is already acidic and warm, two qualities that speed up HTC reactions (Berge *et al*., 2011; Hoekman *et al.*, 2011). Recent investigations into the recirculation of process water show some promise. It has been demonstrated that solid product yields, carbon levels within the solid product, dewatering properties of the solid product and HHVs can be improved with process water recirculation (Stemann *et al*., 2013; Uddin *et al*., in press). As HTC production moves from a laboratory to an industrial scale, water recirculation will become much more important as costs of fresh water could be high as well as costs for wastewater treatment. Caution, however, is recommended in cases where the biomass feedstock contains higher levels of heavy metals, as these may accumulate in the process water upon recirculation. The effects of this accumulation are not yet fully understood (Uddin *et al*., in press).

Another potential area of development concerning process water involves possibilities related to using water from other sources, such as leachates, seawater and wastewaters. Although research in this area has just begun, one report shows that variable water quality may have little or no effect on the HTC process (Lu *et al*., 2014). It is clear that usage of pure, clean water will result in high costs as HTC production is expanded, perhaps to the point that pure water cannot be sustainably used in the HTC process (Lu *et al*., 2014). Therefore, this area of inquiry will be important to follow as the scale of HTC plants increases.

Process conditions have an interesting effect on the nature and yield of liquid products, and this is evidence of the complex nature of the HTC process. At low reaction severity there is less water produced, low levels of acetic acids and relatively higher levels of precipitates in the form of sugars (Hoekman *et al*., 2011; Kruse *et al*., 2013; Yan *et al*., 2010). This can be explained by the temperature sensitive nature of dehydration and decarboxylation. At higher temperatures and longer residence times, there is increased water formation by dehydration as well as higher acetic acid formation by dehydration. This is also linked to higher levels of decarboxylation, which helps to explain higher CO_2 levels at higher reaction severity. The lower temperature presence of higher levels of sugars is evidence that these products of hydrolysis are not being dehydrated to as high a degree as they are at higher temperatures. However, as temperatures and residence times increase, there is not always such a marked decrease in precipitates as one might expect. Although levels of most sugars decrease, there is a slight increase in glucose and a noticeable increase in a degradation product of monosaccharides, 5-hydroxymethyl furfural (5-HMF) (Yan *et al*., 2010). This seems counterintuitive until one realizes the nature of lignocellulosic biomass. At lower temperatures, hemicellulose is rapidly decomposed into sugars through hydrolysis. At high levels of process severity, this hemicellulose gets ‘used up’ quickly. However, as temperatures exceed roughly 250°C, cellulose begins to degrade at more significant levels, resulting in the observed increases in glucose and 5-HMF. Up to that point, comparatively more cellulose and essentially all the lignin remains in a solid state and follow a different reaction pathway. For practical reasons, this may be why some choose 250°C to be an upper limit of HTC (Funke & Ziegler, 2010). After this point, evidence of hydrothermal liquefaction may begin to be seen. Kruse *et al*. classify HTC as occurring between 160-250°C, and hydrothermal liquefaction as occurring between 300-350°C. What occurs in the range of 250-300°C has yet to be clearly classified.

2.5.3 Solid products

As can be inferred from the discussion so far on gaseous and liquid products, the nature and yield of solid products of HTC are strongly influenced by both process conditions and type of feedstock. In general, the solid product of HTC is a char that is elementally similar to lignite or sub-bituminous coal (Funke & Ziegler, 2010). In terms of its chemical characteristics, it is higher in carbon and relatively lower in both hydrogen and oxygen than the original feedstock, evidence of both dehydration and decarboxylation. As process severity increases, solid yields will decrease; however, H/C and O/C ratios will also decrease, resulting in greater energy densification and higher heating values (Berge *et al*., 2011; Hoekman *et al*., 2011; Sevilla & Fuertes, 2009). It has been noted, however, that slightly higher H/C ratios are associated with the HTC char of food waste and anaerobically digested sewage sludge (Berge *et al*., 2011). Slightly higher H/C and O/C ratios of HTC char compared to natural coal have been widely reported and are evidence of the presence of a higher number of functional groups in HTC char (Funke & Ziegler, 2010; Hu *et al*., 2010). This will be an important factor in later discussion. Typical values are shown in Figure 5.

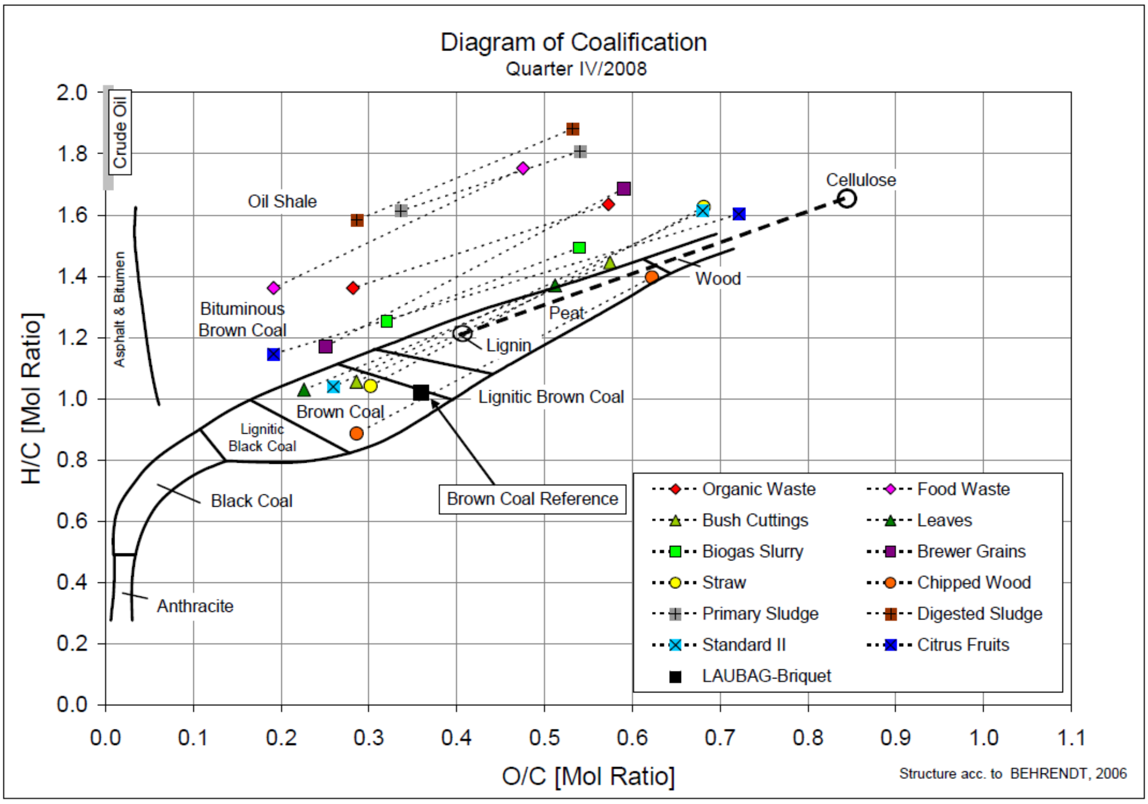


Figure 5: Typical coalification diagram (Ramke *et al*., 2009)

Structural and chemical characteristics of HTC char have been of particular interest in recent years. It has been known for some time that HTC char obtained from non-structural carbohydrates are generally agglomerations of micrometre-sized carbon spheres that result in a sponge-like network of particles; although, feedstock and process conditions determine the exact nature of particle morphology (Titirici *et al*., 2007). Further, HTC particles exhibit different chemical properties in the core and on the shell of the particle. These differences are related to the fact that fairly stable oxygen bonds are established in the core, and less stable oxygen bonds are found on the shell (*ibid*.). Accordingly, the shells tend to be hydrophilic and the cores hydrophobic (Figure 6).

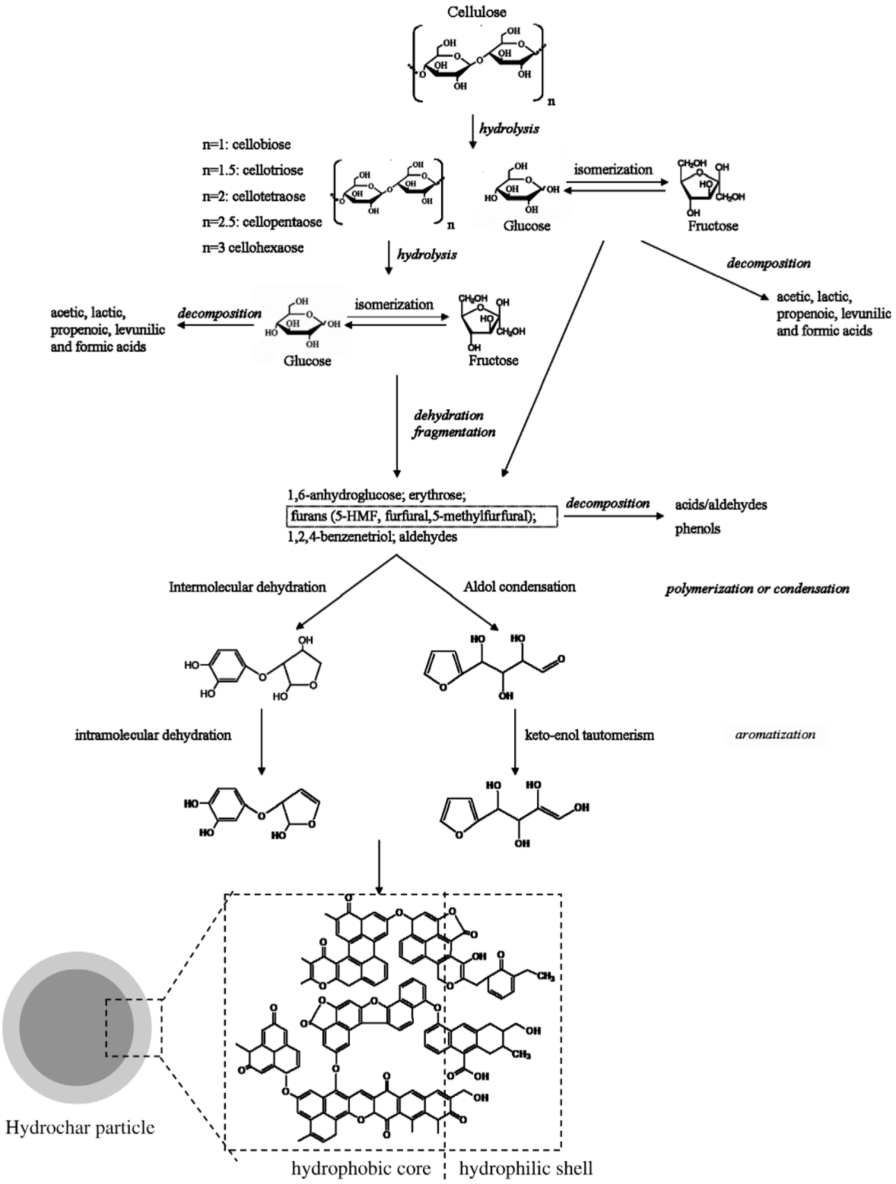


Figure 6: Formation of HTC char from cellulose (Sevilla & Fuertes, 2009)

However, longer carbonization times will result in a decrease in shell functional groups, rendering the particles more hydrophobic (He *et al*., 2013). This has been combined with observations that HTC char particles possess interesting carbon nanostructures (Titirici & Antonietti, 2010) that can be manipulated through the use of different templates or additives. For example, iron ions and iron oxide nanoparticles can both catalyse HTC reactions and influence the morphology of the resulting carbon nanomaterials. Further, the porosity of particles can be increased by performing HTC in the presence of nanostructure silica templates. In addition, the presence of Te nanowires during HTC can direct the formation of carbonaceous nanofibres. Next, hybrid materials can be produced such as carbon nanospheres and nanocables in the presence of noble metal nanoparticles and $AgNO_3$, respectively.

Finally, carbonaceous nanostructures can be doped with nitrogen to create a complex sponge-like mesoporous system by either adding nitrogen-containing substances to the HTC reaction or by using feedstock materials already high in nitrogen (*ibid*.).

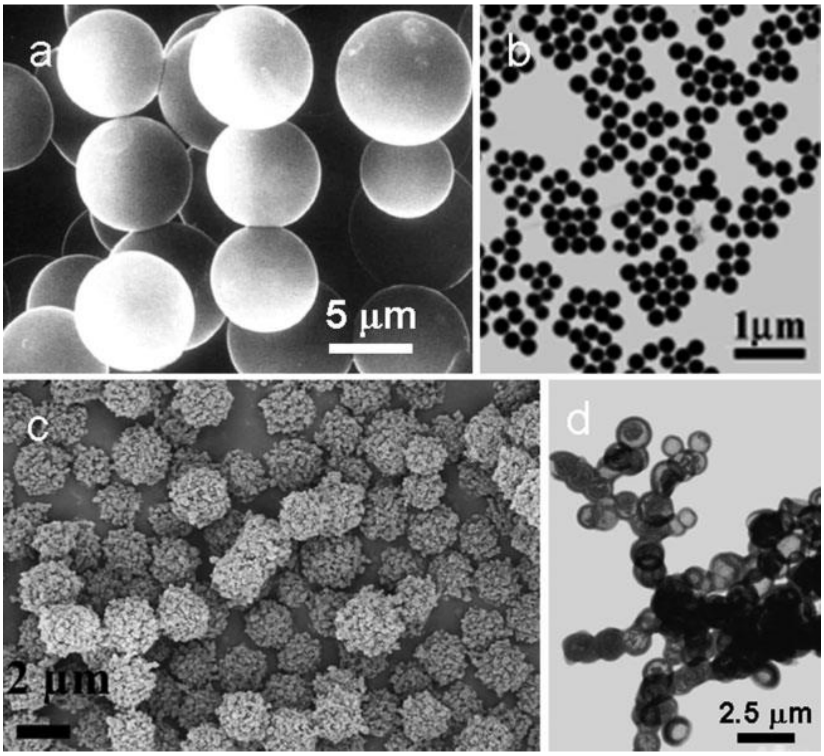


Figure 7: a) Scanning Electron Microscope (SEM) image of monodispersed hard carbon spherules. b) Transmission Electron Microscope (TEM) image of carbon spheres. c) SEM images of carbonaceous materials. d) TEM image of hollow spheres (Hu *et al*, 2010)

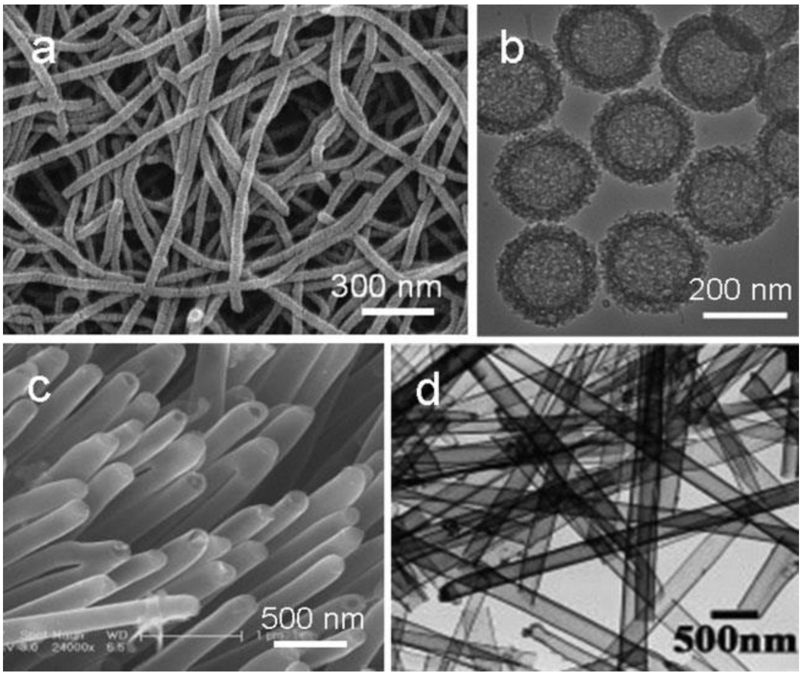


Figure 8: a) SEM image of carbon nanofibres. b) TEM image of hallow carbon materials. c,d) SEM and TEM images of carbonaceous polymer nanotubes (Hu *et al*, 2010)

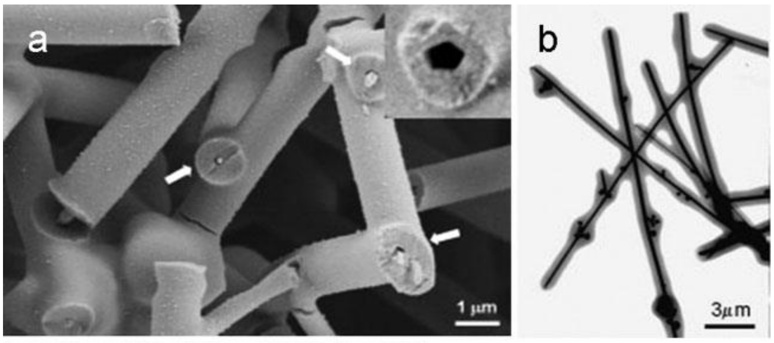


Figure 9: a,b) SEM and TEM images of nanocables with encapsulated, pentagonal-shaped silver nanowires (Hu *et al*, 2010)

For carbohydrates with structure, particularly those arising from biomass or waste, HTC char products can be quite different. The key determinant of the HTC solid product will be the nature of the crystalline cellulose structure. For so-called ‘soft’ or non-textured biomass, such as pine needles, that lacks an extended crystalline cellulose scaffold, a fairly unstructured collection of hydrophilic and water-dispersible spherical nanoparticles ranging from 20-200μm are observed. Particle size is a factor of process conditions. For ‘hard’ biomass made from crystalline cellulose, such as oak leaves, the original structure of the carbon material, for the most part, is maintained. However, this structure is penetrated by a continuous, sponge-like system of nanopores. This is often referred to as an ‘inverted’ structure of the ‘soft’ biomass (Hu *et al*., 2010; Libra *et al*., 2011; Titirici & Antonietti, 2010).

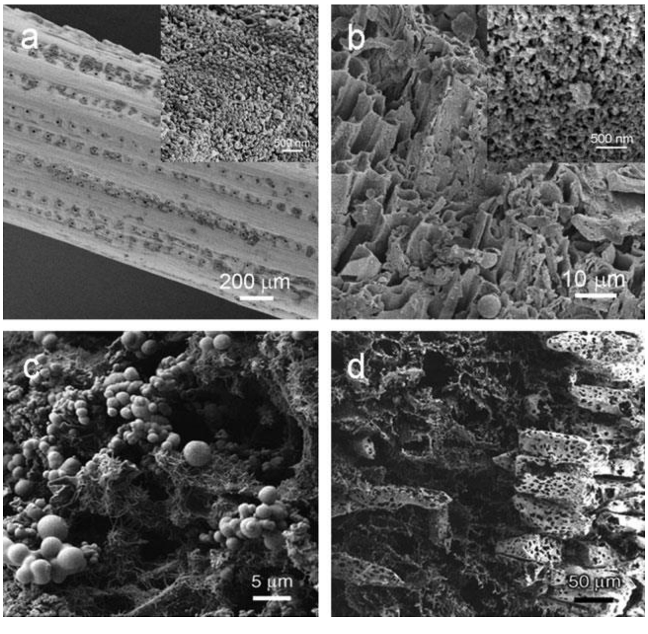


Figure 10: a) SEM image of the ‘soft’ biomass of pine needles before the HTC process; the inset shows an SEM image of after HTC process. b) SEM image of ‘hard’ biomass of oak leaf after the HTC process treatment. C) SEM image of the coexistence of carbon spheres and a microstructured biological tissue. D) SEM image of carbon scaffold replicating of the nonsoluble carbohydrates in rice (Hu *et al*, 2010)

The overall result of this discussion is that chemical properties, morphology and functionality of HTC solid products can be controlled, meaning carbon materials can be designed for a wide range of applications. One of the key observations that can be made at this time is that as chemical and morphological properties can be manipulated, so can the area and nature of the surface of the HTC char. Of equal importance is that not only can materials be designed for novel applications, but HTC can be viewed as a cheaper and more sustainable method of producing important carbon materials that have traditionally been manufactured by other means and from non-renewable or scarce resources (Titirici & Antonietti, 2010).

2.5.4 Char characterization

Given the variability in char production and char characteristics, an International Biochar Initiative has been established to regulate the nomenclature of process and product parameters (Libra *et al.*, 2011). While this initiative works with the production of biochar for soil amendment activities in mind, the guidelines set down offer a way of looking at the HTC industry as a whole. Table 4 provides a summary of important parameters discussed so far in this report and alludes to others that will feature in subsequent discussions.

Table 4: Overview of important HTC feedstock, process and product parameters (Libra *et al.*, 2011)

Parameter	**Method of measurement or quantification**
Feedstock	• Source, type and composition • Type of pre-processing
Process conditions	• Temperature • Residence time • Rate of heating • Reactor pressure • Solid yield • Type of post-processing
Chemical composition	• Elemental compositions • Molar H/C and O/C ratios • Volatile content • Ash content • Mineral content (N, P) • Presence of heavy metals and other substances
Physical characteristics	• Surface area • Bulk density • Particle size distribution • Porosity
Chemical characteristics	• pH • Electrical conductivity • water-holding capacity • Water drop penetration time • Cation exchange capacity • Calorific value
Biological tests	• Biodegradability • Earthworm avoidance / attraction • Germination inhibition

2.6 Potential applications of HTC products

2.6.1 Fuel

Using biomass and waste as fuel is inherently difficult. As the scope of biofuels expands, so too do the challenges associated with the heterogeneity of these fuel sources. Most renewable energy sources tend to be wet and quite diverse in terms of shape, density, heating value, grindability as well as ash, volatile and oxygen content, among other factors. As a result, transport and storage become complicated and costly endeavours. In addition, there is often a need for some type of pre-treatment to convert biomass and waste into some form of intermediate fuel that would be more suited to thermochemical conversion technologies (Yan *et al*., 2010). Drying, for instance, can sometimes be very costly in terms of energy consumption. HTC offers the advantage of providing a relatively homogeneous solid fuel that has properties approaching that of lignite coal (Kruse *et al*., 2013; Libra *et al*., 2011; Ramke *et al*., 2009; Stemann & Ziegler, 2011; Yan *et al*., 2010). Yan *et al*. (2010) report the HTC of Loblolly Pine resulted in char that contained 55-90% of the mass and 80-95% of the energy value of the original feedstock. Likewise, Ramke *et al.* (2009), after testing a wide variety of organic waste, determined that 60-90% of the gross calorific value of feedstock could be maintained in the HTC char. Although total mass of solid product was not given, they report that 75-80% of carbon was maintained in the solid phase. As well, there was noticeable reduction in H/C and O/C ratios, suggesting appreciable overall mass loss.

One of the world's first industrial scale HTC plant was opened by AVA-CO2 Schweiz AG in 2010 and currently produces a CO_2 -neutral HTC char (referred to as bio-coal and biochar) with a calorific value of 25 MJ/kg from a variety of waste streams. Annual production is roughly 8000 tons per year from approximately 40000 tons of biomass and 10000 m^3 of water, which is both recirculated and easily treated upon use. In general, feedstock comes from waste streams that are relatively high in sugars, starches, cellulose and hemicellulose. These include agricultural residues, oil-bearing plant plantation residues, fruit industry waste, spent grains, malting waste, as well as waste coffee grounds and tea leaves. Feedstock that is relatively high in protein or lignin is avoided for reasons related to process efficiency or environmental issues. The AVA-CO2 HTC process occurs at 220°C at approximately 20 bar of pressure. AVA-CO2 boasts several advantages over biomass including higher suitability for long term storage, reduced storage, transport and drying costs, easier and more stable fuel combustion, higher carbon efficiency, lower fuel sulphur and nitrogen levels, hydrophobicity, ease of grinding and lower ash melting point (AVA CO2 Schweiz AG, 2014). These results and advantages are consistent with those found in the literature for fuels in laboratory conditions (He *et al.*, 2013; Liu *et al.*, 2014; Reza *et al.*, 2012).

2.6.2 Energy storage

Through the use of specific feedstock, formation templates, additives, variable process conditions and post-treatment options, HTC char morphology can be directed towards many desired ends. Of particular importance is an ability to create HTC particles with high porosity and desirable morphology. The result can be a complex, compact substance with very high surface area. For a carbon-based material, this is incredibly useful as some important modern energy storage methods are based on the fact that energy can be stored using carbon as electrode material. Typically, activated carbon or graphite from fossil sources is used for such purposes. However, there are several reviews of how HTC char materials can be used for superior energy storage capacity in supercapacitors and Lithium ion batteries (Hu *et al*., 2010; Sevilla *et al*., 2012; Titirici & Antonietti, 2010; L. Zhao *et al*., 2010). In addition, the high surface area and attractive surface structure make HTC char particles superior fuels in indirect carbon fuels cells. Typically, more surface area means a greater rate of oxidation in the anode. As interest in fuel cells is currently topical, especially in relation to renewable fuels, there is a great deal of interest in the capabilities of HTC char particle oxidation (Titirici & Antonietti, 2010). While this line of research is still relatively new, there is growing interest in the fact that "hydrothermally treated biomass can indeed act as a potential fuel for decentralized energy generation with an overall zero-emission balance of CO_2" (*ibid*.). Further possibilities for energy storage will be discussed in relation to the effectiveness of HTC material as a gas adsorbent (Section 2.6.5).

2.6.3 Biochar

HTC chars have been examined as potential soil additives to increase soil fertility and create carbon sinks. However, a definitive conclusion on both of these claims seems to be lacking. Regarding soil fertility, it seems many of the generalizations have been extended from the benefits noticed from soils enhanced with pyrolysis biochar, such as enhanced water-holding capacity, increase in cation exchange capacity, stimulation of certain types of microbial growth and attraction of earthworms (Libra *et al*., 2011). In fact, some research suggests that while HTC char may have some positive effect on fungal growth in soils, there may be neutral or negative effects on plant growth under certain conditions (Rillig *et al*., 2010). It is an intriguing idea that such a multipurpose substance as HTC can be used as a soil additive, particularly in areas of degradation or low fertility by creation of a *terra preta*. However, since there are so many parameters involved in determining soil quality (*ibid.*), caution must be exercised in determining either positive or negative effects of biochar at this time.

The argument concerning the ability of HTC char to create a "CO_2 disposal" industry, (Titirici & Antonietti, 2010) one which effectively results in the sequestering of atmospheric CO_2, is equally dubious at this time. It is indeed attractive to think that a carbon sink can be created through the HTC of biomass and waste. The idea is that instead of these substances degrading into a form of carbon that finds its way to the atmosphere naturally, a more or less permanent, solid form can be produced and then contained. This leaves the current biomass to grow and ingest the CO_2 that has so far been accumulating from past industrial activities. The result is a negative carbon balance. However, it is unclear at this time just how long HTC char will remain sequestered and what the mitigation potential of HTC char really is. At this time, an accurate accounting of the effects of HTC char on GHG mitigation is lacking. In addition, estimates of how long biochar will remain in soils or other sinks vary widely (Libra *et al.*, 2011). Therefore, while the role of HTC biochar as both a soil additive and carbon sink remains intriguing, further study in this area is needed.

2.6.4 Catalysts

There is a role for HTC materials to play as heterogeneous catalysts themselves or as catalyst supports (Titirici, 2013). In particular, control of the large surface areas, porosity, complex architectures and functionalization of HTC materials makes them attractive in a variety of applications. In addition to the discovery of novel applications, HTC materials can replace current catalysts that are derived from non-renewable sources, exhibit lower activity or are produced at higher cost (*ibid.*). Carbon materials loaded with noble metal nanoparticles have been created when HTC is performed in the presence of noble metal salts (Titirici, 2013; Xu *et al.*, 2007). In particular, these substances have been proven to catalyse the hydrogenation of phenol to cyclohexanone in one step. This is a significant improvement over the two-step process that is usually involved or the one step process that has traditionally taken place under harsh conditions and using commercially available catalysts. In addition, carbonaceous nanofibres derived from HTC have been successfully loaded with noble metal nanoparticles to create a hybrid catalyst for the conversion of CO to CO_2 in a low temperature environment (Titirici & Antonietti, 2010). This offers possibilities for further improvements of fuel cells, among others (Titirici, 2013). Next, a strong acid catalyst has been synthesized through relatively low temperature HTC that results in greater reaction efficiency and can replace catalysts normally obtained through high heat treatment and a two-step process (Liang & Yang, 2009). Further still, the ability to produce nitrogen-doped HTC materials that can function as catalysts or catalyst supports offers even further possibilities of reaction selectivity and higher conversion efficiency in a number of processes (Libra *et al*., 2011). Lastly, a carbon doped-TiO_2 composite produced under hydrothermal conditions showed enhanced photocatalytic activity and is currently being investigated as a material that can boost solar photoconversion efficiency (Titirici, 2013).

2.6.5 Adsorbents

Since the effectiveness of a given adsorbent is so highly dependent on its porosity, surface area and surface chemistry, there has been great interest in examining the use of relatively low-cost, ‘green’ HTC materials as adsorbents due to the ability to control porosity, surface area and degree of surface functionality (Roman *et al*., 2013). Several studies have recently demonstrated the high effectiveness of HTC material to selectively adsorb undesirable substances from both air and water. The environmental applications of this area of research seem very promising.

Gas adsorbents

Recent studies indicate that activated carbon produced from HTC carbons derived from glucose and rye straw can effectively store methane at high pressure (Falco *et al*., 2013; Titirici *et al*., 2012). This effectiveness was comparable to other top performing materials in this regard. It is believed that further tailoring of pore size density through KOH activation or HTC temperature optimization can result in an even more effective CH_4 storage material (Falco *et al*., 2013). Similarly, high density hydrogen storage was demonstrated by activated carbon materials produced from the HTC of renewable organic materials (furfural, glucose, starch, cellulose and eucalyptus sawdust) (Sevilla *et al*., 2011). The implication of these studies is that both gases have the potential to be stored at levels that make them more effective as portable fuels in fuel cells. It is well known that both gases can be used effectively as fuel. The main barrier to broader use thus far has been storage. While investigations into the practical use of HTC carbons as compact storage devices are still relatively new, results seem very promising.

One of the boldest claims of HTC researchers is that char material shows the most promising opportunity so far to capture and store CO_2. Clearly, the ability of HTC material to capture two important gases has already been demonstrated. However, in order to effectively capture CO_2, any sorbent will need to be of low cost and high availability, be able to uptake large amounts of CO_2 at a high rate of sorption, have good selectivity between CO_2 and other gases (such as nitrogen) and have the ability to be easily regenerated (Titirici, 2013). Despite this relatively tall order, HTC-derived materials represent a very good alternative according to each of the mentioned criteria.

CO_2 adsorption by materials derived from HTC has been demonstrated to an excellent degree (Falco *et al*., 2013; Sevilla & Fuertes, 2012). Again, biomass that underwent HTC was shown as a good precursor for the production of an activated carbon that showed a promising ability to capture CO_2. Additionally, this can be done relatively quickly and cheaply in comparison to other sorbents and with high CO_2/N_2 selectivity (Falco *et al*., 2013). Further research of carbon materials containing or doped with nitrogen (Sevilla *et al*., 2012; Zhang *et al*., 2012) shows that increasing functionality and tailoring porosity has led to the "unprecedented large CO_2 capture capacities" (Sevilla *et al*., 2012). In both of the above cases, the initial feedstock was both cheap and renewable.

Liquid adsorbents

Research into the use of HTC materials as adsorbents of pollutants from water have focused mostly on increasing the surface functionality of HTC particles. Specifically, a number of studies have found that HTC particles have a relatively large number of oxygen-containing functional groups on the particle surface, especially carboxylic groups, that increase their adsorption behaviour towards a number of common water pollutants. In addition, a few studies have indicated that the number of oxygen-containing functional groups of HTC particles can be enhanced by pre- and post-treatment of materials, as well as manipulation of HTC process conditions. A number of studies also suggest that adsorption behaviour of HTC char is dependent upon such factors as the pH of the aqueous solution, the amount of char in relation to liquid, and the amount of contact time (Regmi *et al*., 2012).

The feasibility of HTC char as an absorbent of heavy metals was first observed by Liu *et al*. (2009). Their studies indicated that the irregular surface of HTC char particles in addition to a relatively high number of oxygen-containing groups (carboxylic, lactone and phenolic hydroxylic) lead to good removal of lead from water (Liu & Zhang, 2009). This was later followed up by observations that HTC char derived from pinewood could also remove copper effectively from wastewater, and in a superior manner to chars derived from pyrolysis (Liu *et al.*, 2010). Importantly, both studies reported that adsorption behaviour was influenced by pH, with adsorption efficiency highest at a pH of approximately 6 and decreasing as pH increased or decreased. At approximately the same time, it was reported that lead could be removed from water at 30 times the efficiency if carbon material was treated with a solution of acrylic acid before carbonization (Demirbas & Arin, 2002). These results also proved that HTC chars could demonstrate adsorption behaviour “well beyond ordinary sorption capacities” of commonly employed adsorbents (*ibid.*).

One researcher interested in boosting the number of oxygen-containing functional groups of HTC chars showed that carbon nanocomposite materials could exhibit superior adsorption of lead and chromium by taking advantage of the morphology of the scaffold material and the functionality of the carbon source material (Chen *et al.*, 2011). Another showed that a simple thermal treatment in air after HTC could increase functionality and adsorption of lead and cadmium (Chen *et al.*, 2011). Yet another showed that cold activation with KOH can increase the sorption ability of HTC char by increasing functionality (Regmi *et al.*, 2012). Still another showed that post-treatment with hydrogen peroxide could increase functionality and adsorption of lead, copper, cadmium and nickel (Xue *et al.*, 2012). This study also indicated that a common waste material (peanut hull) could be used successfully as feedstock. Further to this, Alatalo *et al.* (2013) demonstrated that heavy metal adsorbent HTC materials could be derived from such common waste materials as anaerobically digested municipal sludge and industrial sludge from the pulp and paper industry. Highlights of the above-mentioned research are summarized in Table 5. It should be noted, however, that adsorption tests were conducted on single metal ion aqueous solutions, with the noted exception of Xue *et al.* (2012). The result reported in that study for Pb(II) removal in a multi-metal solution was slightly lower than that reported for the single metal solution shown in Table 5. For the multi-metal solution, the removal rate for Pb(II), Cd(II), Cu(II) and Ni(II) was 16.45, 0.21, 1.22 and 0.07 mg/g respectively. Further research on sorption behaviour of HTC char outside of laboratory situations is currently lacking.

Table 5: Experimental conditions and results of heavy metal adsorption studies

Source	HTC conditions			Post-treatment	Pre- or post-treatment Objective	Reported removal efficiency (mg g^{-1})
	Material	Temperature (°C)	Residence time (hours)			
(Liu & Zhang, 2009)	Pinewood	318	0.33	Drying at 100°C for 24 hours		4.25 Pb(II)
(Liu & Zhang, 2009)	Rice husk	318	0.33	Drying at 100°C for 24 hours		2.40 Pb(II)
(Liu *et al.*, 2010)	Pinewood	300	0.33	Drying at 105°C for 24 hours		4.21 Cu(II)
(Alatalo *et al.*, 2013)	Anaerobically digested sludge	200	24	Drying overnight at 80°C		11.27 Pb(II)
(Alatalo *et al.*, 2013)	Pulp and paper industry sludge	200	24	Drying overnight at 80°C		11.78 Pb(II)
(Demir-Cakan *et al.*, 2009)	Glucose treated with Acrylic acid	190	16	Drying overnight at 80°C	Increase oxygen-containing groups	351.4 Pb(II) 88.8 Cd(II)
(Chen *et al.*, 2011)	Glucose	180	24	Drying at 50°C for 12 hours; Thermal treatment in air for 5 hours at 300°C	Increase oxygen-containing groups	326.1 Pb(II) 150.7 Cd(II)
(Xue *et al.*, 2012)	Peanut hull	300	5	Drying at 80°C		1.04 Pb(II)
(Xue *et al.*, 2012)	Peanut hull	300	5	Drying at 80°C; treatment with H_2O_2 for 2 hours; drying at 80°C	Increase oxygen-containing groups	22.82 Pb(II)
(Chen *et al.*, 2011)	Attapulgit clay@Carbon (from glucose) Nanocomposite	160	48	Drying	Increase oxygen-containing groups	263.83 Pb(II) 177.74 Cr(IV)
(Ramke *et al.*, 2009; Regmi *et al.*, 2012)	Switchgrass	300	0.5	Air drying		4.0 Cu(II) 1.5 Cd(II)
(Regmi *et al.*, 2012)	Switchgrass	300	0.5	Air drying Cold treatment with KOH and overnight drying at 105°C	Increase surface area and oxygen-containing groups	31.0 Cu(II) 34.0 Cd(II)

In addition to studies on adsorption of heavy metals, experiments have also shown that HTC chars can effectively adsorb certain organic pollutants as well as uranium. First, HTC chars from poultry and animal (swine) waste proved to be effective adsorbents of phenanthrene, a dangerous polycyclic aromatic hydrocarbon, as well as bisphenol A and 17α-ethinyl, two endocrine disrupting chemicals (Sun *et al*., 2011). Second, hazelnut shells that underwent HTC and activation with KOH at high temperature (600°C for 2 hours) demonstrated an ability to adsorb methyl blue dye (Unur, 2013). Due to the measured increase in particle surface area, porosity, pore volume and functionalization, this suggests an ability of HTC chars to adsorb a range of polar and nonpolar organic pollutants from aqueous solutions. Third, HTC char derived from switch grass could perform as an effective adsorbent of uranium (VI) from groundwater (Kumar *et al*., 2011). In addition, pine needles in a citric acid solution that underwent HTC were efficient adsorbents of U (VI) from an aqueous solution (Zhang *et al*., 2013). Moreover, the ability to regenerate the adsorbent and recover U (VI) was demonstrated in a mild solution of HCl. Effectiveness of the HTC chars to act as adsorbents in each of the above cases was due to the diversity of the HTC material structure as well as the presence of functional groups on HTC particles.

2.7 HTC plant design considerations

To date, very little HTC is done outside of laboratories or pilot-scale projects. In these cases, focus is usually somewhat limited to the success of the HTC reaction in single batches and less attention is paid to pre- and post-treatment as well as how continuous production can be efficiently maintained. In industrial-sized plants, however, there will be tremendous focus on the investment and production costs associated with all three of these areas (Titirici, 2013). Indeed, it is a contemporary issue to determine the best way to scale up HTC projects to an industrial scale. There are several key issues that need to be considered during plant design.

The feedstock will be an important factor in plant design for several reasons. First, choosing a location for the plant may be related to transport distances of the feedstock as well as availability. Second, certain types of biomass feedstock may have a cost, whereas using waste streams may either be free or even have a tipping or gate fee associated with them. Third, pre-treatment of feedstock may be necessary and costly. This need has less to do with physical reasons related to the reaction than practical reasons related to process efficiency (*ibid*.). Larger particle feedstock can successfully undergo HTC, but it generally needs higher temperatures or longer residence times. Related to this is the fourth issue, the feeding system. In general it will be the feeding system that determines the needed size of raw material particles. The feeding system will likewise be a factor of the type and scale of the reactor used. This will be discussed subsequently. Lastly, the amount of water in the feedstock will be an important factor. In general, the more water in the feedstock, the less energy efficient the process will be as heat will be needed to warm that water. This issue is also related to water re-use and heat transfer that will be discussed later. At the same time, feedstock with high water content is generally easier and cheaper to handle in terms of a feeding system. Clearly, several variables are interacting in a successful plant design.

The reactor type chosen is also an important decision. This choice will generally be related to a decision to either number up (or increase throughput by having a number of reactors similar to a pilot-scale design) or scale up (making everything on a larger scale). This choice will likewise be dependent upon choosing either a batch or continuous reactor. While both reactor types have advantages and disadvantages that have been discussed in the literature (Titirici, 2013), an important observation to be made at this time is that continuous reactors necessitate the use of feeding systems that work against pressure. As well, it is important to note that more efficient heat transfer and better conservation of energy are associated with continuous reactors (Erlach & Tsatsaronis, 2010; Stemann & Ziegler, 2011).

This leads to the next important consideration in HTC plant design – heat recovery. The three main issues related to energy are the heat required to achieve reaction temperatures, the heat required to dry the wet HTC char and the heat possibly lost in the form of reaction gas (Stemann & Ziegler, 2011). Through recirculation and re-use of gaseous and liquid products, an efficient process can be achieved. In general, this is more easily achieved in the relatively compact continuous reactor types, such as tubular reactors or continuously stirred tank reactors (Titirici, 2013). Erlach and Tsatsaronis (2010) propose a model that aims at using internal heat sources as efficiently as possible (Figure 11). This is similar to that proposed by Stemann and Ziegler (2011). In both cases, use of external natural gas can be limited by re-use of process liquids and gases. HTC plant efficiency will also decrease with increasing water content of feedstock, as energy will be necessary to heat this water and less internal water can be re-used (Stemann & Ziegler, 2011). In addition, external steam could be acquired from a related process, such as a CHP plant, and waste heat from the HTC process could be employed for space heating in other parts of a facility, thereby increasing overall efficiency (Erlach & Tsatsaronis, 2010).

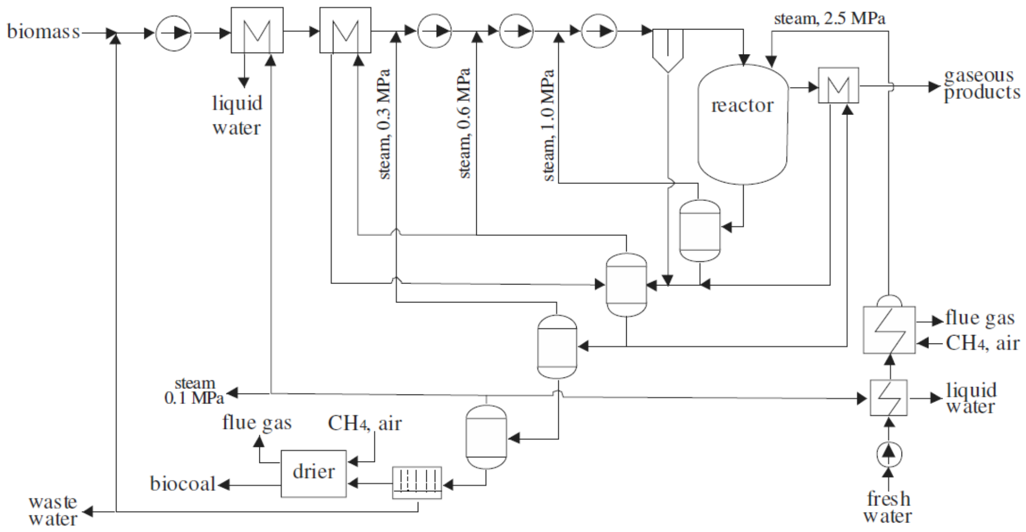


Figure 11: Model of proposed HTC plant design (Erlach & Tsatsaronis, 2010)

One final area of consideration in plant design is the treatment or disposal of waste streams. While re-use of process liquids will reduce both the amount of fresh water required and wastewater generated, some amount of liquid waste will be produced. And as stated previously, efforts could be made to recover any valuable materials from this liquid stream. In the end, however, typical water treatment will suffice in handling HTC plant discharge. In terms of gaseous waste, efforts could be made to recover or oxidize minor compounds, such as carbon monoxide, hydrogen and gaseous hydrocarbons. This remains an area for further study as larger-scale HTC plants begin production in the coming years.

2.8 Best available technology for industrial-scale HTC

While many endeavours are underway to take HTC out of the laboratory and into mainstream industry, as yet very few groups can demonstrate industrial-scale production. For this reason, the following discussion is limited to companies that have already shown an ability to process more than 1000 tons of biomass feedstock annually in pilot or demonstration plants. In addition, each of the following groups mentioned offer operational designs with the capacity to handle more than 10 000 tons of raw biomass annually.

2.8.1 SunCoal Industries

This group’s patented CarboREN technology offers municipal and industrial customers an ability to convert a range of biomass into HTC char (called SunCoal) in a variety of forms, including powder, granules and pellets. Modular units are employed that can be designed to customer specifications. The company offers complete service from project inception to implementation which includes feasibility studies, development, approvals, turnkey construction, production launch, testing, process optimization, after-sales service, training and maintenance. The company claims to achieve the most energy efficient process of all the major HTC plant designs (SunCoal Industries, n.d.).

The CarboREN process begins with biomass being received and stored, depending on its composition, in order to facilitate automatic loading. Next it is crushed to a uniform 60 mm size to facilitate feeding and impurities are removed, such as stone, metal or plastic. The biomass is then mixed with low pressure steam and recycled process liquid in order to increase temperature and pressure. This is followed by further mixing with high pressure steam to achieve reaction conditions of 200°C and 20 MPa in the continuous reactor, which is mixed by an electric stirring mechanism. The biomass slurry enters the top of the reactor while the HTC slurry is removed from the bottom as converted particles with greater density sink to the bottom of the reactor. Mixing of highly converted particles with unconverted feedstock is minimized by a combination of agitation and longer residence times (6-12 hours for continuous reactors compared to approximately 5-10 hours for batch reactors). The HTC slurry is then depressurized to atmospheric conditions, cooled, and mechanically dewatered. Low and high pressure steam and liquid product are recycled in the process. Thermal drying and further post-treatment equipment, such as a pellet production line can be added according to customer requirements. The process ends with storage and transport.

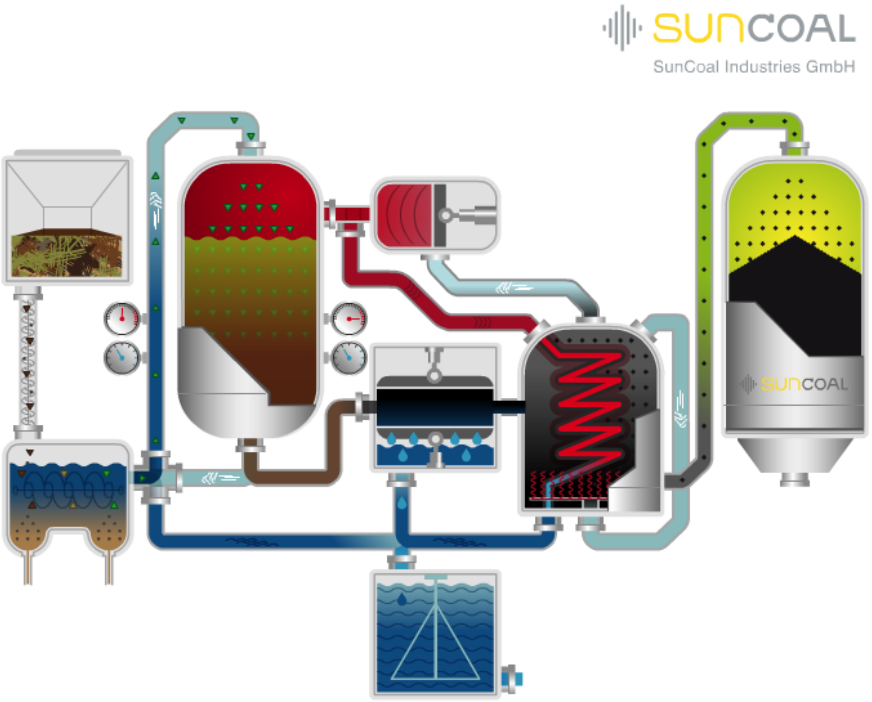


Figure 12: The CarboREN Process (*ibid.*)

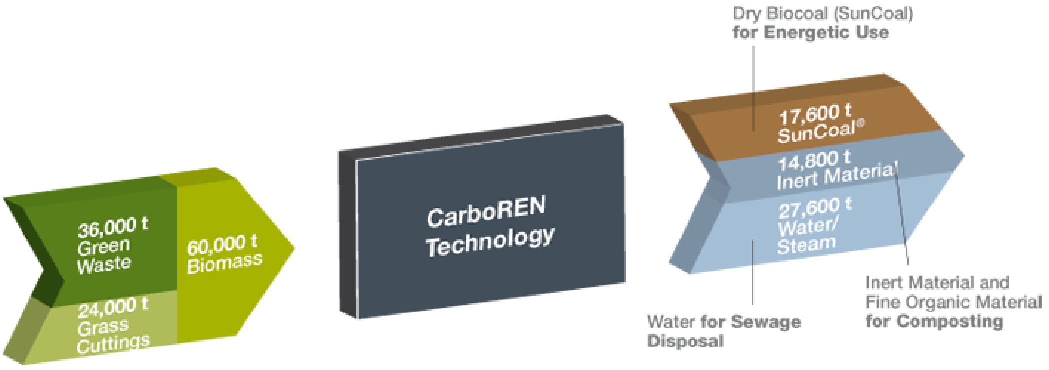


Figure 13: Mass balance of CarboREN Process (*ibid.*)

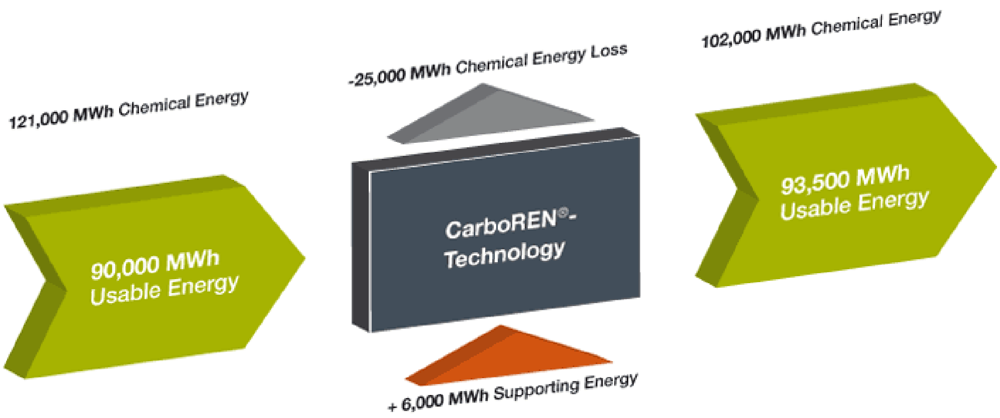


Figure 14: Energy balance of CarboREN Process (*ibid.*)

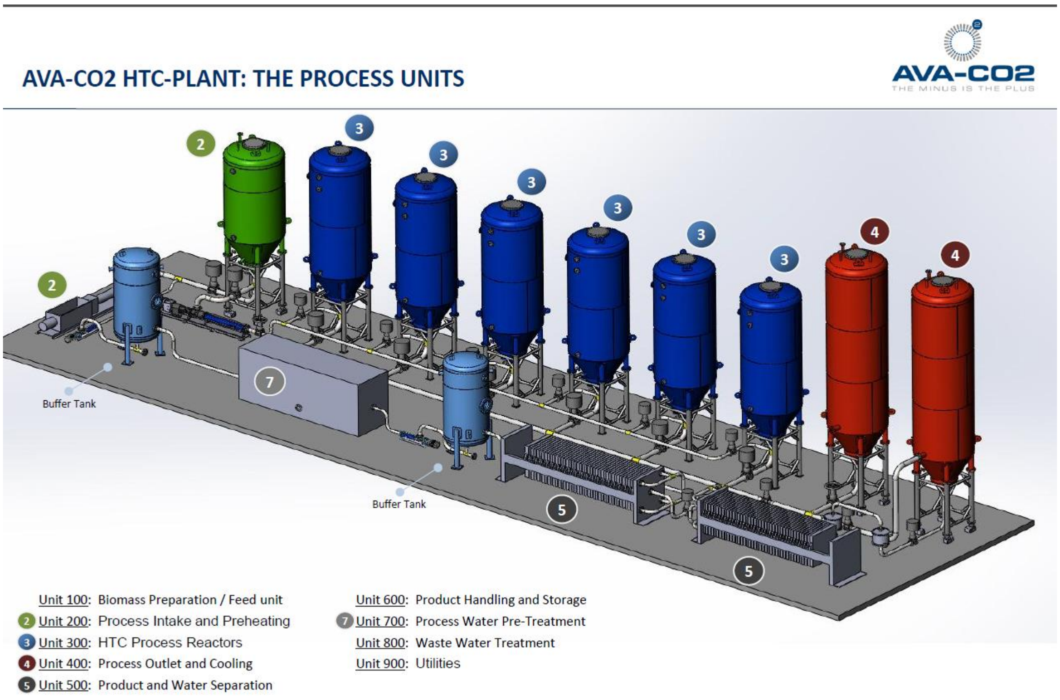
Table 6: SunCoal reactor characteristics

HTC Reactor Characteristics	
Manufacturer	SunCoal
Began operations	2008; industrial-scale capacity since 2012
Reactor name	CarboREN
Reactor type	Continuous
Capacity	Approximately 50000 tons per year raw biomass
Heating system	Steam
Process conditions	200°C; 2 MPa; 6-12 hours
Cost	Estimated at € 3 million
Contact	Email: info@suncoal.com Website: www.suncoal.de
Remarks	Reactor designed to accommodate range of biomass (20-75% TS). Plans for industrial plant to process up to 60 000 tons per year of raw biomass. Plant designs available for capacity of 375 000 tons per year of raw biomass.

2.8.2 AVA-CO2

AVA-CO2 launched one of the world's first industrial-scale HTC facility in 2010 and now offers worldwide solutions to convert a range of biomass feedstock into HTC char. Modular design means that the industrial-scale units can be numbered up to meet the capacity needs of customers. AVA-CO2 uses a great deal of familiar industrial technology that should not present great burdens to construction or maintenance staff. The company offers a complete range of services from project implementation to operation (AVA CO2 Schweiz AG, 2014).

The AVA-CO2 process begins with biomass preparation similar to that described for the SunCoal process. The second step involves the intake and preheating of feedstock in a designated mixing tank by combining feedstock with both high and low pressure (recycled) steam as well as recycled process liquid. The slurry is transferred to one of several batch reactor tanks upon reaching reaction conditions (Table 7). Reactions in the reactor tanks can be facilitated by a stirring mechanism or the use of catalysts. Once conversion is complete, the HTC slurry is drained from the reactor tank by gravity and transferred by pump to high and low pressure flash tanks where process energy can be stored until needed for preheating. Cooling of the HTC solid product also takes place before it moves to mechanical dewatering and further processing if necessary.



AVA-CO2 HTC-PLANT: THE PROCESS UNITS

Unit 100: Biomass Preparation / Feed unit
② Unit 200: Process Intake and Preheating
③ Unit 300: HTC Process Reactors
④ Unit 400: Process Outlet and Cooling
⑤ Unit 500: Product and Water Separation
Unit 600: Product Handling and Storage
⑦ Unit 700: Process Water Pre-Treatment
Unit 800: Waste Water Treatment
Unit 900: Utilities

Figure 15: AVA-CO2 Process (Kläusli, 2014)

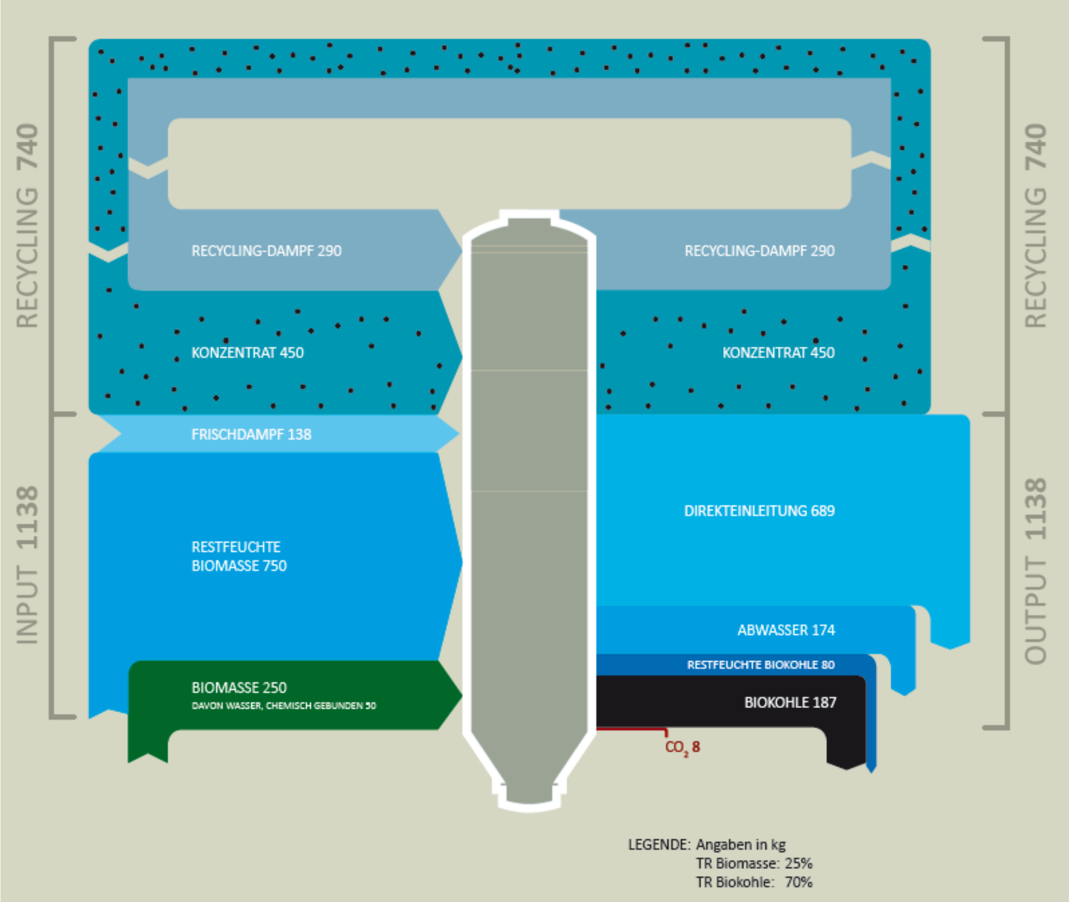


Figure 16: AVA-CO2 mass balance (Kläusli, 2014)

Table 7: AVA-CO2 reactor characteristics

HTC Reactor Characteristics	
Manufacturer	AVA-CO2
Began operations	October 2010
Reactor name	HTC-0
Reactor type	Batch
Capacity	10800 DM tons / year (40000-50000 tons raw biomass); 8040 tons / year of biocoal
Heating system	Steam
Process conditions	220-230°C; 2.2-2.6 MPa 5-10 hours
Cost	Estimated at € 6-10 million
Contact	Thomas Kläusli Email: tk@ava-co2.com Website: www.ava-co2.com
Remarks	Rector designed to accommodate a range of biomass (25-75% DM). Some pre-processing of input material is necessary. Some process liquid and steam are recirculated. Liquid effluent is transferred to a wastewater treatment facility.

2.8.3 TFC Engineering

Very little has been published about the TF.C-Carbon-5000/10-12 reactor of TFC Engineering and company officials did not respond to requests for information despite comments that they would do so. It is assumed that the continuous reactor will function in a similar manner to that already described for SunCoal Industries.

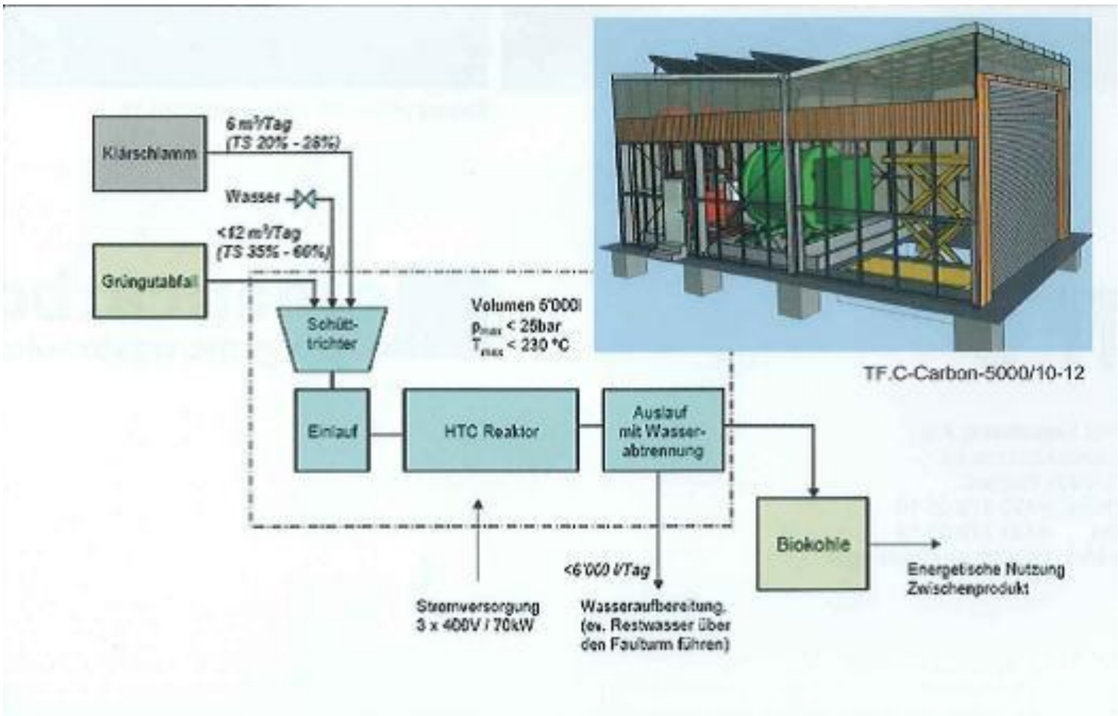


Figure 17: TFC Engineering process (Robbiani, 2013)

Table 8: TFC Engineering reactor characteristics (*ibid.*)

HTC Reactor Characteristics	
Manufacturer	TFC Engineering, Kelag AG
Began operations	December 2012
Reactor name	TF.C-Carbon-5000/10-12
Reactor type	Continuous
Capacity	10 000 tons per year raw biomass
Heating system	Oil
Process conditions	200-230°C; 2-2.5 MPa; 3-4 hours
Cost	€ 2.9 million
Contact	Roland Rebsamen Email: info@tfc-engineering.li Website: www.tfc-engineering.li
Remarks	Reactor is designed to accommodate a combination of wet biomass (20-60% TS). Start of industrial operations was delayed due to problems associated with the reactor.

2.8.4 TerraNova Energy

TerraNova Energy solutions are designed in a compact way to allow easy, decentralized, local installation. Scaled-up modules are designed to handle approximately 1 200 tons of raw biomass annually, but can be numbered up to handle up to 12 00 tons per year. The company offers an interesting tubular design with innovative heat recovery systems. TerraNova Energy has operated a demonstration plant in Kaiserlautern, Germany since 2010.

The process in this case begins with biomass pre-processing to achieve particle size that is optimal for feeding into a continuous reactor. Under pressure, the biomass feedstock flows through a winding tube connected to a heat exchanger in a contrary flow to the HTC product leaving the reactor in a parallel tube (Figure 18). Oil is used as the heat recovery agent. At the moment the biomass enters the reactor it has been preheated to near reaction temperature and pressure (Table 9). At the same time it is combined with a catalyst or additive, and fed into the continuous reactor. An agitator ensures a homogenous mixture and char particles slowly sink to the bottom of the tank, from where they are released through the heat exchanger. The process ends with mechanical dewatering and possible post-treatment depending on customer needs.

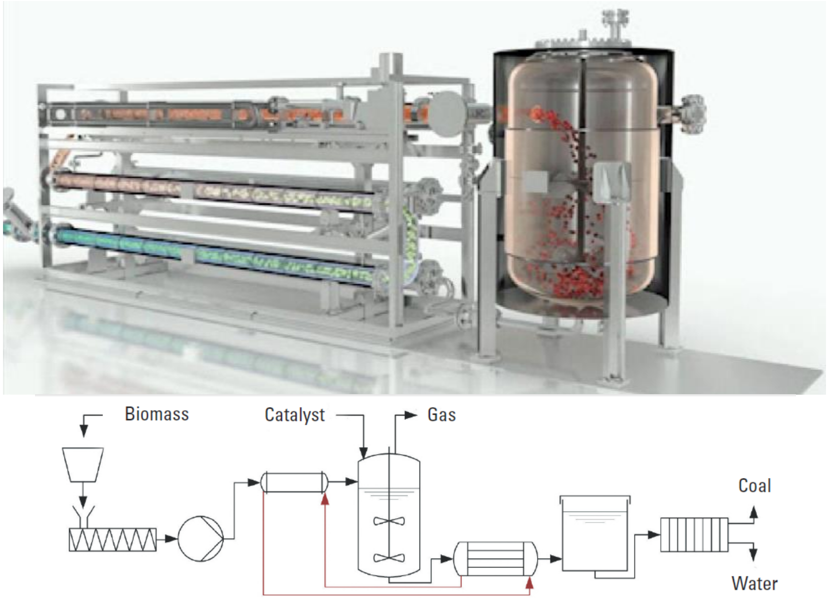


Figure 18: TerraNova Energy Process (TerraNova Energy, n.d.)

Table 9: TerraNova Energy reactor characteristics

HTC Reactor Characteristics	
Manufacturer	TerraNova Energy
Began operations	April 2010
Reactor name	Not available
Reactor type	Continuous
Capacity	E.g. 8000 tons per year of wet sludge Units can be numbered up for higher capacity
Heating system	Oil
Process conditions	200°C; 2-3.5 MPa; Approximately 4 hours
Cost	Estimated at € 5-6 million
Contact	Email: info@terranova-energy.com Website: www.terranova-energy.com
Remarks	Rector designed to accommodate a range of biomass. Very compact design results in minimal demands for space.

2.8.5 Ingelia S.L.

Ingelia S.L. has operated an industrial-scale HTC prototype facility since 2010 and was the first to operate a continuous reactor on an industrial scale. Designs are modular that can be readily numbered up and designed to customer specifications. Ingelia offers an Inverted Flow Reactor and has developed a unique Pressure and Temperature Control System. The nature of this system is to regulate process gaseous and liquid products within the reactor in order to facilitate their use in preheating. Detailed information about the control system is proprietary. The reactor itself operates in much the same manner as continuous reactors already described.

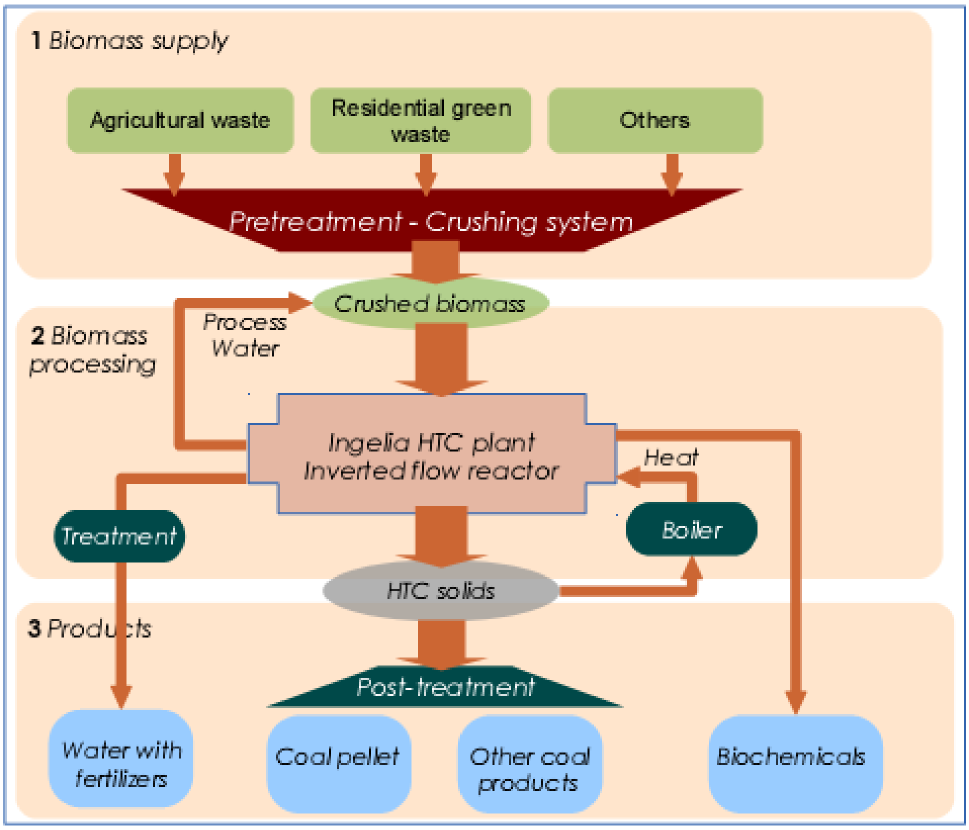


Figure 19: Ingelia Process (Hitzl, 2014)

Table 10: Ingelia reactor characteristics (Hitzl, 2014)

HTC Reactor Characteristics	
Manufacturer	Ingelia S.L.
Began operations	2010
Reactor name	Inverted Flow Reactor
Reactor type	Continuous
Capacity	Each module is designed to process 6000 tons of wet biomass annually. Modules can be numbered up to meet customer's capacity needs.
Heating system	Steam from Biomass / Bio-coal boiler (auto consumption)
Process conditions	180-220°C; 1.7-2.4 MPa; 4-8 hours
Cost	Unknown
Contact	Email: ingelia@ingelia.com Website: http://www.ingeliahtc.com/English/index.htm
Remarks	Rector designed to accommodate a range of biomass. The company is part of a large study in Europe to investigate the feasibility of HTC of a number of municipal waste streams.

3 THE CURRENT STUDY

Waste sludge materials make interesting candidates for HTC treatment for a number of reasons. First, they are abundant and have few competing uses. Typically, they can be landfilled, reused in agricultural or composting operations, incinerated, gasified, or treated in order to be used in a variety of soil enhancement projects such as construction, landscaping or landfill capping. Importantly, biodegradable, non-hazardous sludge of all types will, effectively, no longer be accepted in landfills throughout the European Union after 2016 (EUR-Lex, n.d.), so there is a great need to find alternatives for their disposal or use. Second, they have high water content that causes a number of difficulties during traditional treatment. For instance, transport and disposal may be expensive; dewatering or drying may be necessary and costly; or leachates may require management. The reduction or management of water within sludge is seen as a key issue for any efficient use, reuse or disposal program (Zhao *et al*., 2014). This high water content is not a barrier to HTC treatment, but is in fact a requirement to some extent. Third, solid matter within sludge materials generally has a high organic content, making them excellent candidates for HTC. Lastly, HTC may offer the possibility to treat sludge materials in a sustainable, more energy- and carbon-efficient manner than traditional sludge treatment methods.

3.1 Aims

HTC models and demonstration plants exist that show the possibilities of scaling up operations for a range of municipal and industrial clients. Most demonstrate a general feasibility of converting various waste streams into solid fuels, but no studies have fully identified all of the opportunities and challenges associated with large-scale operations, especially with respect to long-term economic, environmental and social sustainability. Likewise, the scope of analysis has been either too narrow or has not given full consideration to the wide range of opportunities and challenges associated with industrial-scale HTC production. It is also generally accepted that any analysis of HTC must be specific to the potential feedstock under consideration. The purpose of this study will be to compare alternative treatment options of anaerobically digested municipal sewage sludge (ADS) and industrial sludge from the pulp and paper industry (PPS) with respect to the three pillars of sustainability.

Four scenarios will be established for each waste stream:

1. Sludge to disposal, treatment or incineration
2. Sludge to drying, followed by incineration
3. Sludge to HTC, followed by incineration
4. Sludge to HTC, followed by drying, pelletizing and sale

First, a characterization of the waste streams will be performed to provide sufficient background information and allow for meaningful comparison of the scenarios. Second, models will be developed of mass, energy and economic flows for each scenario. The ultimate goal will be to develop a value of the net cost or revenue related to processing one ton of sludge for each scenario. Third, a range of opportunities and challenges related to HTC treatment will be explored. When possible, related costs or revenues will be estimated. In some cases optimistic and conservative estimations will be included. Part of this discussion will include a theoretical analysis of HTC char combustion. Lastly, conclusions on profitability will be drawn and recommendations will be made.

3.2 Feedstock materials

While sludge materials from numerous waste streams have some similar characteristics, they are sufficiently heterogeneous that some information concerning their nature and how they are produced is necessary in order to invite comparison. Furthermore, it has already been established that the precise nature of a feedstock will have a significant effect on the outcome of the HTC process. To this end, a characterization of two specific feedstock materials will follow. These sludge feedstock materials, of course, are products of processes that have their own feedstock materials that can vary temporally, geographically and as a result of differing socio-economic contexts. At the same time, it is hoped that these characterizations can serve as representative samples of their classes within the Finnish context to at least a reasonable extent.

3.2.1 Pulp and paper industry sludge

Figure 20 shows a typical process that produces a mixed sludge in a pulp and paper mill. It should be noted that the sludge products differ for pulp only mills as well paper only mills. Further, sludge materials from mills that use de-inked or recycled paper differ still. As well, some mills keep a strict separation of primary and secondary sludge, possibly utilizing different treatment or disposal methods. In the case being considered, wastewater comes from a pulp and paper mill such as Kaukas in Lappeenranta, Finland.

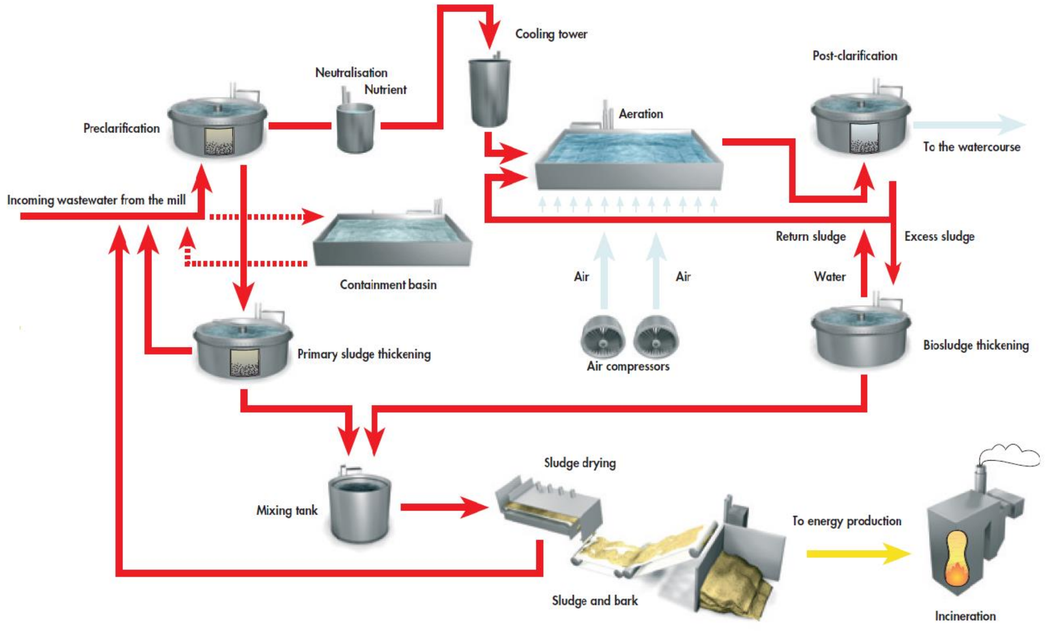


Figure 20: Production of pulp and paper sludge (UPM, 2013)

In this situation wastewater is comprised of substances derived from virgin wood processing and various process chemicals. Primary clarification (labelled Pre-clarification in Figure 20) results in a stream dubbed Primary Sludge, which is high in wood fibre content. These are relatively large particles that settle on the bottom of the clarification tank. In total they may represent 60-90 percent of the effluent solid content. The liquid that is separated from the Primary Sludge then goes to Secondary treatment, which involves aeration and biological treatment. During biological treatment protozoa and microbes feed on the organic component of the effluent. At the same time oxygen is pumped into the tank for aeration. After settling, excess sludge (essentially made up of dead organisms) is removed, creating Secondary Sludge (also known as biosludge). Both Primary and Secondary Sludge may undergo thickening, and then are mixed and dewatered. Mechanical dewatering is commonly achieved by a mechanical press (screw or belt filter) or centrifuge. Thermal drying can also be employed (UPM, 2013).

At this stage the solid content is approximately 25%. In many mills, such as Kaukas, the mixed sludge is mixed with bark to even out the moisture, and then it is incinerated in a biomass boiler. In other mills, mixed sludge may be further dewatered and dried before incineration on its own or with other biomass substances. It is well-known that reducing the water content of pulp and paper sludge is difficult and expensive due to its structure. Choices regarding the level of dewatering or drying needed are often determined by the nature of the furnace in which it is incinerated. It is commonly accepted throughout the industry that the energetic benefits of burning such a wet feedstock are approximately equal to the overall cost of doing so. In effect, the process of incineration is one which reduces the absolute amount of sludge to be disposed. In this case, it is turned into ash which can be disposed of more easily and cheaply. Other alternatives include composting and soil enhancement. At the Kaukas mill, part of the sludge is used to both construct and cover the mill's own landfill site. In total, Kaukas produced 19,000 wet tons of mixed sludge in the wastewater plant in 2012 (Liimatainen, 2013).

The pulp and paper sludge under consideration in this study is characterized in Table 11. Bark has been added to the table for comparison and to aid in subsequent calculations. Values have been calculated based on the equations that follow.

$$HHV_{DAF1} = \left(78.31C + 359.32\left(H - \frac{O}{8}\right) + 22.12S + 11.87O + 5.78N\right) kcal/kg \tag{1}$$

$$HHV_{DAF2} = (HHV_{DAF1} / 238.8)\ MJ/kg \tag{2}$$

$$LHV_{DAF} = (HHV_{DAF2} - (l * M_{H2O}/M_{H2}) * H/100)\ MJ/kg \tag{3}$$

$$LHV_{DB} = LHV_{DAF} * (1 - Ash/100) \tag{4}$$

$$LHV_{AR} = LHV_{DB}\ (1\text{-}Moisture/100)\text{-}\ (l\text{-}Moisture/100) \tag{5}$$

where,

M_{H2O} = molar mass of water from combustion of hydrogen (g/mol) = 18.015

M_{H2} = molar mass of combusted hydrogen (g/mol) = 2.016

l = latent heat of evaporation for water (at 25°C) = 2.441 MJ/kg

Table 11: Characterization of PPS

Parameter	**Bark, dried (spruce #3158)**			**Raw pulp and paper sludge, after dewatering or drying**			**HTC char from pulp and paper sludge, after dewatering or drying**			
	DAF%	**DB% a**	**AR%**	**DAF%**	**DB% b**	**AR%**	**DAF%**	**DB% b**	**AR%**	**AR%**
C	51.10	49.9	47.28	47.67	34.80	20.88	50.65	35.20	21.12	31.68
H	6.04	5.9	5.59	5.89	4.30	2.58	6.04	4.20	2.52	3.78
O	42.42	41.43	39.25	40.16	29.32	17.59	38.06	26.45	15.87	23.81
N	0.41	0.4	0.38	5.48	4.00	2.40	4.46	3.10	1.86	2.79
S	0.03	0.03	0.03	0.79	0.58	0.35	0.79	0.55	0.33	0.50
Ash		2.34	2.22		27.00	16.20		30.50	18.30	27.45
Moisture			5.25			40.00			40.00	10.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV1 (kcal/kg)	4773.27			4571.69			4923.31			
HHV2 (MJ/kg)	19.99	18.98	17.98	19.14	18.07	10.84	20.62	19.52	11.71	17.57
LHV (MJ/kg)	18.67	17.69	16.64	17.86	17.13	9.30	19.30	18.60	10.19	16.50

a-(ECN, 2012) b-(Areeprasert *et al*., 2014)

3.2.2 Anaerobically digested municipal sludge

Figure 21 shows a typical process that produces a mixed sludge in a municipal wastewater treatment plant. In Europe sludge quality and quantity vary greatly. Estimates range from less than 1 kg of sludge produced annually per population equivalent to more than 30 kg. In Finland it is estimated that production is approximately 18 kg annually per population equivalent (Kelessidis & Stasinakis, 2012). As seen with the treatment of pulp and paper mill sludge, municipal sewage sludge involves primary and secondary treatment. Both Primary and Secondary Sludge are then anaerobically digested, producing a wet cake and methane. This wet cake is usually mechanically dewatered using a press (filter or belt filter) or centrifuge to solid content of approximately 25% (Horttanainen *et al*., 2010). The most common treatment options throughout the EU are agricultural use, landfilling, incineration and composting (Kelessidis & Stasinakis, 2012). As landfilling will be effectively eliminated as an option in 2016, thermal treatment with energy recovery is expected to increase not only in Finland, but around the world as the other treatment options become increasingly competitive and expensive industries (Horttanainen *et al*., 2010).

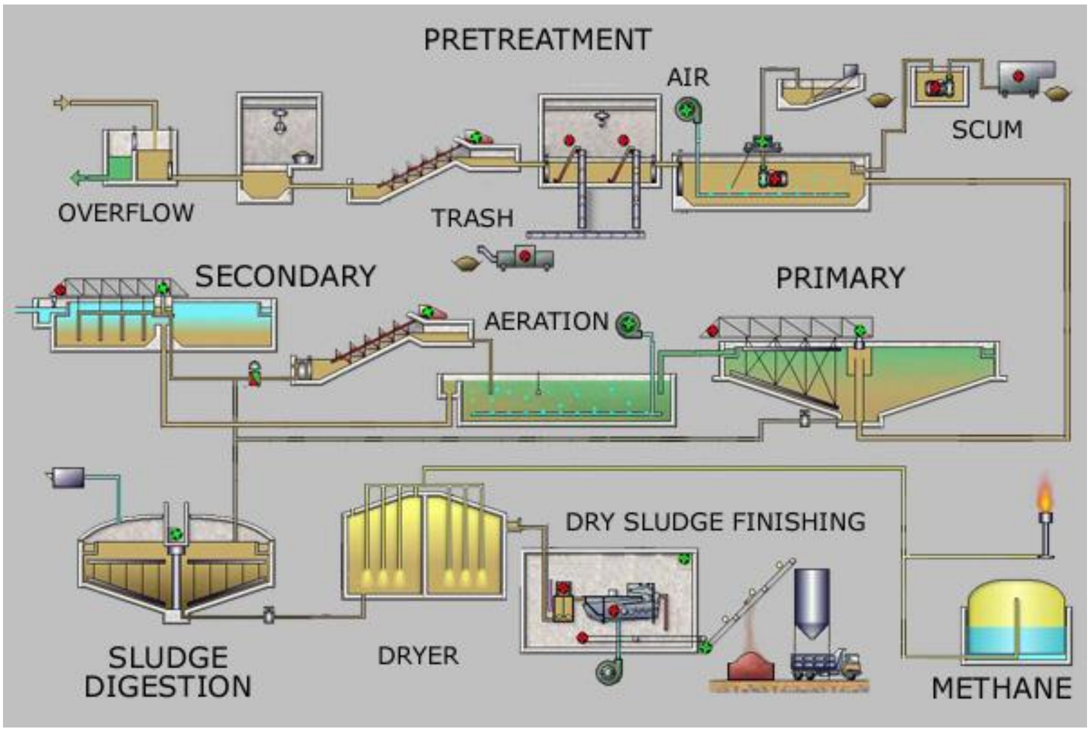


Figure 21: Production of anaerobically digested municipal sludge (Wikipedia, 2014)

Thermal treatment of anaerobically digested municipal sludge is usually achieved by co-firing with coal, in cement industry kilns, in Municipal Solid Waste incinerators or in suitable other mono- and co-combustion furnaces (Horttanainen *et al*., 2010; Kelessidis & Stasinakis, 2012). In these situations, the profitability of thermal technologies is often dependent on establishing sludge reception fees. At the same time, these thermal treatment options are not employed in situations where phosphorous recovery is needed. These last two facts will have key relevance in further discussions.

The capacities of wastewater treatment facilities vary greatly to the extent that no typical value can be accurately discerned. In the region of South Karelia, Finland, approximately 13 212 tons of sludge (19% solid matter) is produced annually (Havukainen *et al*., 2012). The majority of this is treated at the Toikansuo wastewater treatment facility in Lappeenranta and then converted to compost.

The anaerobically digested municipal sludge under consideration in this study is characterized in Table 12. Bark has been added to the table for comparison and to aid in subsequent calculations. Values have been calculated based on Equations 1-5.

Table 12: Characterization of ADS

Parameter	Bark, dried (spruce #3158)			Raw anaerobically digested municipal sludge, after dewatering or drying			HTC char from anaerobically digested municipal sludge, after dewatering or drying			
	DAF%	DB% a	AR%	DAF%	DB% c	AR%	DAF%	DB% c	AR%	AR%
C	51.10	49.9	47.28	36.74	24.89	17.42	41.32	25.86	18.10	23.27
H	6.04	5.9	5.59	7.06	4.78	3.35	6.62	4.14	2.90	3.73
O	42.42	41.43	39.25	48.83	33.08	23.16	44.09	27.59	19.31	24.83
N	0.41	0.4	0.38	5.77	3.91	2.74	6.12	3.83	2.68	3.45
S	0.03	0.03	0.03	1.61	1.09	0.76	1.85	1.16	0.81	1.04
Ash		2.34	2.22		32.25	22.58		37.42	26.19	33.68
Moisture			5.25			30.00			30.00	10.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV1 (kcal/kg)	4773.27			3867.55			4232.61			
HHV2 (MJ/kg)	19.99	18.98	17.98	16.20	15.02	10.52	17.72	16.56	11.59	14.90
LHV (MJ/kg)	18.67	17.69	16.64	14.66	13.98	9.05	16.28	15.66	10.23	13.85

a- (ECN, 2012) c-(Escala *et al*., 2012)

3.3 Treatment options for sludge

Four treatment scenarios have been created for pulp and paper as well as anaerobically digested municipal sludge. The first two represent scenarios that are typical for both feedstock materials. The third is a modification of the second which includes HTC treatment. This HTC treatment differs for each of the sludge materials due to the limited nature of data available for industrial-scale HTC. HTC treatment of PPS will be based on a model of PPS treatment in a continuous reactor constructed by SunCoal Industries. HTC treatment of ADS will be based on a model of ADS treatment in a batch reactor constructed by AVA-CO2. In both situations, calculations will be based on 50 000 tons of raw, wet sludge treatment per year (20-25% DM). It is generally agreed upon within the industry that a successful economic model of HTC at an industrial level cannot be developed below this capacity. As will be shown, operational parameters of the HTC treatments as well as the composition of the feedstock materials will differ so greatly as to make meaningful comparison between the two technologies impossible. It is hereby assumed that neither HTC technology is superior to the other. The last scenario also involves the same HTC treatment, but ends with the creation of solid fuel products that are sold rather than utilized by the producer. For this reason the first scenario is viewed primarily as a disposal scenario, the second and third are viewed as utilization scenarios, and the fourth is viewed as a production scenario. Each one will involve different responsibilities on the part of the producer of the sludge that will be described in turn. Of course, many more possible scenarios exist. These four scenarios were designed to invite comparison of common treatment alternatives to those involving the latest possibilities of industrial-scale HTC. Each scenario will involve the tracking of flows of mass, energy, costs and revenues as accurately as possible. However, due to the proprietary nature of many of the treatment alternatives, estimates are often used. It was also deemed important to set boundaries of the analyses involved in this study. Figure 22 shows the extent of these system boundaries.

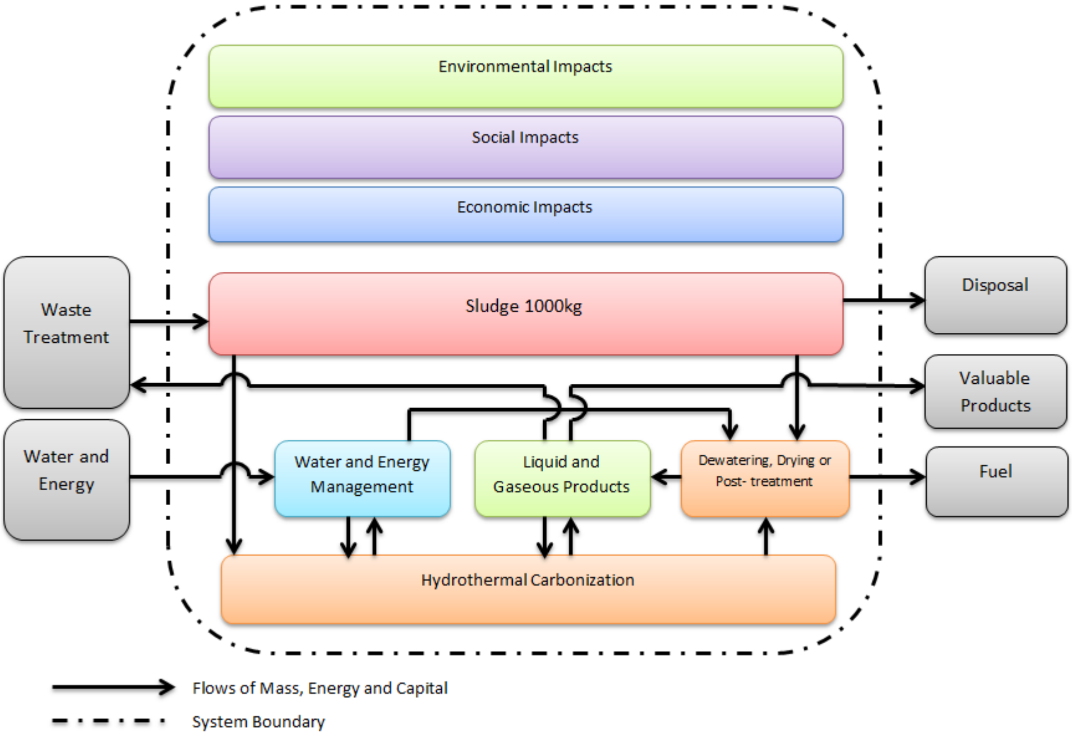


Figure 22: System boundaries of the current study

3.3.1 Scenario 1 - Disposal and other treatment

There are a number of options available to sludge producers that fall into the category of disposal and other treatment. For the purposes of this study, these options will include composting, agricultural or forestry use, landscaping, construction and industrial use, and direct incineration. Each option will naturally have either direct or indirect costs and may be exercised by either the sludge producer or external waste management company. For example, the UPM Kaukas mill manages its own waste at the company-owned Tuosa landfill site. There, pulp and paper sludge is mostly converted into material that can be used for landscaping projects at the landfill itself or around the mill. This material can also be used as capping material for sections of the landfill. In some cases, sludge is dewatered and stored, to be mixed with bark for thermal conversion at a later date (Liimatainen, 2013). Within the same geographic area, municipal sludge undergoes anaerobic treatment and dewatering before being transferred to a municipally-owned compost facility. In both cases, it can be assumed that these activities have an inherent cost. Many sludge producers in Finland, both industrial and municipal, can also opt to pay gate or treatment fees in order for waste management companies to assume responsibility of further treatment.

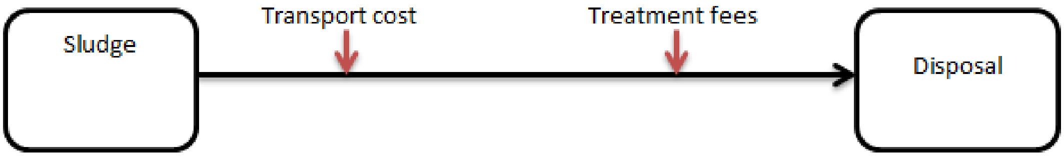


Figure 23: Scenario 1

The costs of disposal or treatment options are difficult to quantify accurately. They will vary depending on transport distances, the water content of the sludge, handling equipment, labour, method and size of operation, as well as governmental regulation and support programmes, among many other factors. In addition, the sludge producers and waste management companies approached during this study refused to divulge financial information regarding their operations due to its proprietary nature. For these reasons, an estimate is necessary. Therefore, it is assumed that disposal and treatment options will fall somewhere in the range of 30-80 € per wet ton of sludge for both feedstocks under consideration based on an assumed 20-25% dry matter content. In addition, an estimate will be made of the cost of directly burning raw sludge materials based on a co-combustion scenario with bark.

3.3.2 Scenario 2 - Incineration

While several options for the thermal treatment of sludge exist, such as gasification or pyrolysis, incineration is by far the most common. The burning of sludge materials has a long history and is nowadays performed in both mono- and co-combustion furnaces of various designs. Due to the high water content of both sludge materials under consideration, it is assumed that some level of mechanical dewatering and drying is necessary before the fuel may be combusted. For the purposes of this study, it is assumed that levels of 70% dry matter by weight are achieved for ADS and 60% for PPS in this scenario before combustion. This decision was based on the availability of data related to HTC treatment and the need to make reasonable comparisons between scenarios. However, this is one important reason why comparisons between the two HTC technologies cannot accurately be made at this time. To accomplish the desired dry matter levels, there is a need of the appropriate infrastructure to achieve these levels. Typically, dewatering is achieved by screws or belt filter presses and will achieve 30% dry matter. Supplemental drying occurs by thermal convection in drums or along drying belts and achieves the final dry matter contents mentioned above.

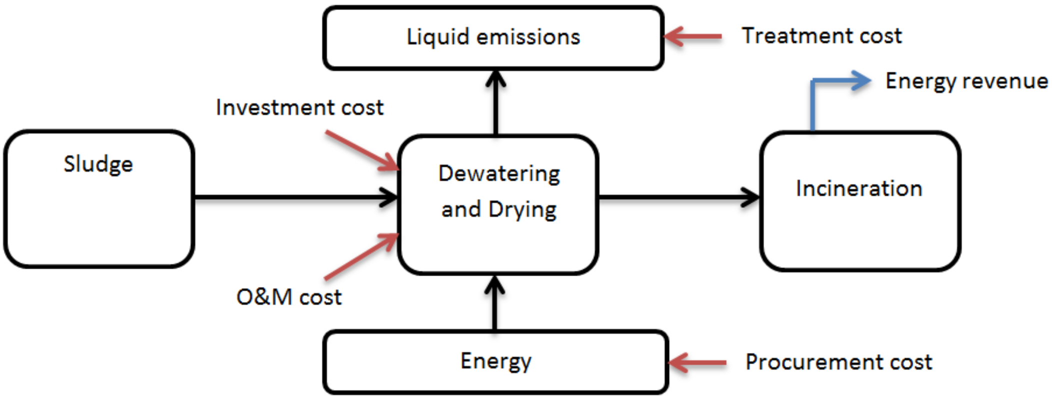


Figure 24: Scenario 2

Costs within scenario 2 will be based on the net present value of investment in a thermal belt drying system for drying. It is assumed that a mechanical belt filter press is already part of the sludge production facility and no further investment is needed. Added to this will be net present value of operation and maintenance costs (assumed to be 5% of investment annually) as well as a treatment fee for effluent liquids. These costs can be expected to be lower than household costs as effluents are returned to the beginning of the sludge production process. They are assumed to be EUR 1 per ton of effluent. Finally, the cost of both electric and thermal energy will be added to determine total costs. It is assumed that electricity has a cost of EUR 100/ MWh and that process steam will cost EUR 50/ MWh. These costs will be compared to estimated revenues from energy production. In order to create accurate estimates of actual energy production, the incineration of sludge will be viewed in a co-combustion simulation with bark.

A biomass boiler was selected as typical of the nature of this co-combustion simulation. The Foster Wheeler 173MW boiler operated by Äänevoima in Äänekoski, Finland is a Bubbling Fluidized Bed (BFB) boiler utilizing bark, sludge, forest residues and peat as fuels. It produces 60.2 kg/s of steam at 105 MPa and 535 °C. In order to achieve these levels of steam, 856 kg of bark must be combusted daily, resulting in just over 20 tons of ash. A co-combustion scenario was devised that maintains the operating parameters of the boiler, but manipulates the amounts of each feedstock. In the co-combustion simulation with raw sludge involving 90% bark and 10% sludge, much higher levels of ash are produced. The cost of handling this ash is assumed to be EUR 100/ m^3. It is likewise assumed that there is no cost in using sludge as a fuel, but that the bark fuel costs EUR 100/ ton. Total ash was assumed to be comprised of 45% of bottom ash and 55% fly ash. Further, bottom ash was assumed to have a density of 600 kg/m^3 and fly ash a density of 300 kg/m^3. By comparing the savings in fuel costs to the additional costs of ash handling, a total cost or profit per ton of sludge or HTC char fired was calculated. Results are shown in Tables 13 and 14. Final cost or profit is adjusted for the yield of the original ton of raw sludge (PPS at 20%DM and ADS at 25%DM). Yields are shown in section 4.1.

Table 13: Cost of PPS sludge and char co-combustion

Feedstock		Fired Mass (Tons per day)	Ash (Tons per day)	Fly ash (m^3 per day)	Bottom ash (m^3 per day)	Fuel cost (€ per day)	Fuel savings per ton of sludge or char fired (€)	Ash disposal cost (€ per day)	Added ash costs per ton of sludge or char fired (€)	Cost /Profit per ton of raw sludge (€)
100 % Bark (95%DM)		856	20.03	36.72	15.02	85600.00	0.00	5174.42	0.00	0.00
90% Bark and 10% Raw PPS (20%DM)	Bark	824	44	80.67	33.00	82400.00	34.78	11366.67	67.31	-32.52
	PPS	92								
90% Bark and 10% Raw PPS (60%DM)	Bark	780	41.65	76.36	31.24	78000.00	87.36	10759.58	64.20	7.71
	PPS	87								
90% Bark and 10% HTC char from PPS (60%DM)	Bark	774	44.34	81.29	33.26	77400.00	95.35	11454.50	73.02	6.25
	PPS	86								

Table 14: Cost of ADS sludge and char co-combustion

Feedstock		Fired Mass (Tons per day)	Ash (Tons per day)	Fly ash (m^3 per day)	Bottom ash (m^3 per day)	Fuel cost (€ per day)	Fuel savings per ton of sludge or char fired (€)	Ash disposal cost (€ per day)	Added ash costs per ton of sludge or char fired (€)	Cost /Profit per ton of raw sludge (€)
100 % Bark (95%DM)		856	20.03	36.72	15.02	85600.00	0.00	5174.42	0.00	0.00
90% Bark and 10% Raw ADS (25%DM)	Bark	826	48.93	89.71	36.70	82600.00	32.61	12640.25	81.15	-48.54
	ADS	92								
90% Bark and 10% Raw ADS (70%DM)	Bark	792	46.91	86.00	35.18	79200.00	72.73	12118.42	78.91	-2.17
	ADS	88								
90% Bark and 10% HTC char from ADS (70%DM)	Bark	784	50.94	93.39	38.21	78400.00	82.76	13159.50	91.78	-2.41
	ADS	87								

3.3.3 Scenario 3 - HTC treatment before incineration

This scenario will mirror that of Scenario 2 with the exception that a hydrothermal carbonization facility will precede dewatering by mechanical belt filter press. In this scenario, thermal drying will not be necessary to achieve desired levels of HTC char dryness (60% DM for PPS and 70% DM for ADS). However, more sophisticated treatment of effluents are assumed to be utilized in order to extract valuable products from the liquid waste stream. Although some valuable materials may also be present in the gaseous waste stream, it is assumed that only carbon dioxide will be released as a gaseous product and that no special gaseous emissions equipment will be utilized. This point will be further explored in subsequent discussion.

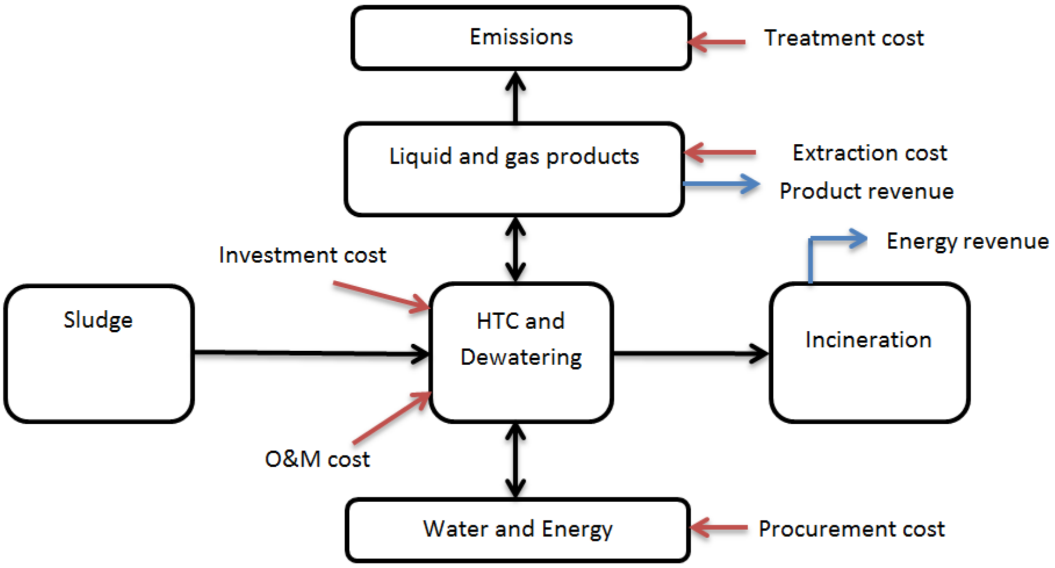


Figure 25: Scenario 3

Costs within this scenario will differ from Scenario 2 in that there will be no cost associated with a thermal dryer. However, the net present value costs of acquiring, operating and maintaining the two different HTC plants, each with a capacity of 50 000 wet tons of sludge (20-25% dry matter), will be included. With regards to the recovery of valuable liquid and gas products, it is assumed, due to a gap in research knowledge, that extraction costs will equal product revenues. Therefore, values will not be calculated. The effect of valuable material extraction on effluent mass is assumed to be negligible for the purposes of cost calculations. These points will be further explored in subsequent discussion. Tables 13 and 14 also show the cost or profit of co-combusting HTC char with bark. Calculations follow methods outlined in Scenario 2. In all other regards, Scenarios 2 and 3 will be identical.

3.3.4 Scenario 4 - HTC treatment before pelletizing

In this scenario, sludge will enter a similar HTC facility to the previous scenario and the product will be dewatered to the same level (60 or 70% dry matter). This will be followed by treatment in a thermal dryer and then pelletization in a pellet production line. The thermal dryer is assumed to be capable of handling approximately 14 000 tons of feedstock per year and the pellet production line of producing approximately 10 000 tons of pellets per year based on 8 000 hours of operation per year. It is assumed that drying will achieve a level of 90% dry matter before pelletization and that no binding agent will be necessary. Therefore, the net present value costs of the acquisition, operation and maintenance (5% of acquisition costs) of the dryer and pellet production line will be included in cost calculations. Another key difference will be that the energy generated from incineration of the pellet will not be included in this scenario. The purpose of this scenario was to present an option for the creation of a value-added end product, in this case an HTC char pellet. It is assumed that a distance of 50 km will apply for the transport of pellets to local end users. Revenue generated from the sale of the HTC char produced in this scenario is assumed to be EUR 22.2/ MWh for the HTC char from PPS and EUR 15.2/ MWh for the HTC char from ADS. The basis of these values is found from the literature (Bagramov, 2010) and based on the price of coal using the following formula:

$$\boldsymbol{Price\ of\ biocoal = Price\ of\ fossil\ coal + (CO_2 allowance * net\ plant\ efficiency)} \quad \textbf{(6)}$$

In this case, the price of coal is assumed to be EUR 28/ MWh, the CO_2 allowance EUR 20/ MWh and net efficiency 36%. The price of the HTC chars under consideration should be adjusted due to high amounts of ash. It is estimated that an ash handling cost of EUR 13/ MWh and EUR 20/ MWh are subtracted from the above price of biocoal for the HTC char of PPS and ADS respectively. These costs are based on a calculation that 1 MWh of HTC char from PPS would generate approximately 50 kg of ash more than 1 MWh of polish bituminous coal #1272 (ECN, 2012) and that HTC char from ADS would generate approximately 78 kg more. Calculations and key assumptions are shown in Table 15.

Table 15: Price estimation of HTC char.

Fuel	**Coal**	**HTC char from PPS (90%DM)**	**HTC char from ADS (90%DM)**
LHV_{AR} (MJ/kg)	30	16.50	13.85
MWh/kg	0.0083	0.0046	0.0038
kg/MWh	120	218.19	259.93
Proportion of ash (AR)	7.97 %	27.45 %	33.68 %
Mass of ash (kg /MWh)	9.564	59.89	87.54
Mass of additional ash (kg /MWh)	0	50.33	77.98
Proportion of bottom ash	45 %	45 %	45 %
Density of bottom ash (kg / m^3)	600	600	600
Mass of bottom ash (kg /MWh)	0	22.65	35.09
Volume of bottom ash (m^3 / MWh)	0	0.04	0.06
Proportion of fly ash	55 %	55 %	55 %
Density of fly ash (kg / m^3)	300	300	300
Mass of fly ash (kg /MWh)	0	27.68	42.89
Volume of fly ash (m^3 /MWh)	0	0.09	0.14
Total volume of ash (m^3 /MWh)	0	0.13	0.20
Cost of ash handling and disposal (€/m^3)	100	100	100
Cost of ash handling and disposal (€/MWh)	0	13.00	20.14
Price of coal (€/MWh)	28.00	28.00	28.00
Carbon reduction support (€/MWh)	0	20	20
Efficiency of facility	36 %	36 %	36 %
Adjusted price of fuel (€/MWh)	28	22.20	15.06
Adjusted price of fuel (€/ton)	233.33	101.74	57.92
Yield of HTC char per ton of raw sludge	-	0.187	0.208
Value of fuel per ton of raw sludge	-	19.02	12.05

Transport is based on a fully loaded lorry capable of carrying a 28-ton load for 50 km. It is assumed that the trip to the destination will be 50 km and that the price of freight will cost EUR 100 per hour plus EUR 1 per km. Loading and unloading included, the journey is expected to last 3 hours. In all other respects, Scenario 4 will be identical to Scenario 3.

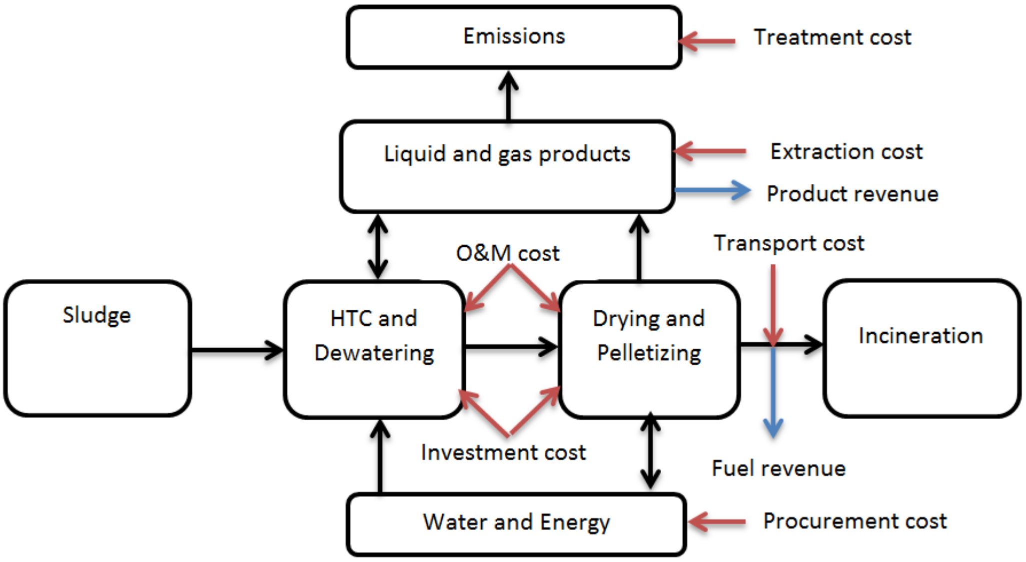


Figure 26: Scenario 4

4 MASS RECOVERY AND PROCESS ENERGETICS

4.1.1 Scenario 1

In Scenario 1, the sludge producer has a number of options for disposal or treatment, as outlined in section 3.3.1. Among these, a company can dispose of or treat the raw sludge at company owned facilities in its entirety. Alternatively, there is the option to pay a handling fee to an external agent for disposal or treatment. In either situation, the entire mass is transferred outside of the defined system boundary, as shown in Figure 27. Within this scenario, one of the treatment options available is incineration with subsequent disposal of ash. It is generally agreed that the energetic cost of incinerating such wet fuels is approximately equal to any energetic gain from the incineration. For that reason, energy calculations were not performed directly. However, mass flows related to ash were tracked in order to perform cost calculations shown in Tables 13 and 14. Incineration resulted in approximately 239 and 314 kg of ash per ton of wet sludge for PPS and ADS, respectively. Assumptions made in section 3.2.2 regarding proportions of bottom and fly ash remain applicable to this scenario. The remaining mass is assumed to be released as wet flue gas.

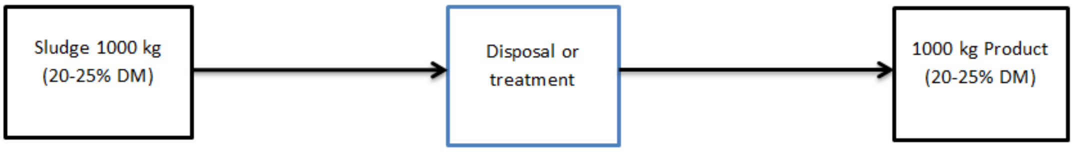


Figure 27: Scenario 1 (PPS and ADS)

4.1.2 Scenario 2

In Scenario 2, differences between the thermal treatment of PPS and ADS become evident. While little comparison will be made in each scenario between the treatments of each type of sludge, it can be stated that PPS is generally easier to dewater and dry than ADS sludge due to the nature of the sludge materials themselves. Results of thermal drying of the sludge materials are shown in Figures 28 and 29. PPS mass and energy flows are extrapolated from data provided by SunCoal Industries and through discussions with representatives from the company (SunCoal Industries, n.d.; Wittmann, 2014). ADS mass flows are extrapolated from data provided by a representative from AVA-CO2 (Kläusli, 2014). Information concerning energy usage during thermal drying is derived from a common usage in the literature that 800 kWh thermal energy and 54 kWh electricity are needed to remove 1 ton of water from ADS using a typical belt dryer (Escala *et al*., 2012). In this scenario evaporated liquid is returned to the wastewater treatment facility and dried product is incinerated. Upon combustion there are approximately 82 and 109 kg of ash per ton of wet sludge for PPS and ADS, respectively. This is based on the fact that one ton of combusted, dried sludge yields 248 and 305 kg of ash for PPS and ADS, respectively.

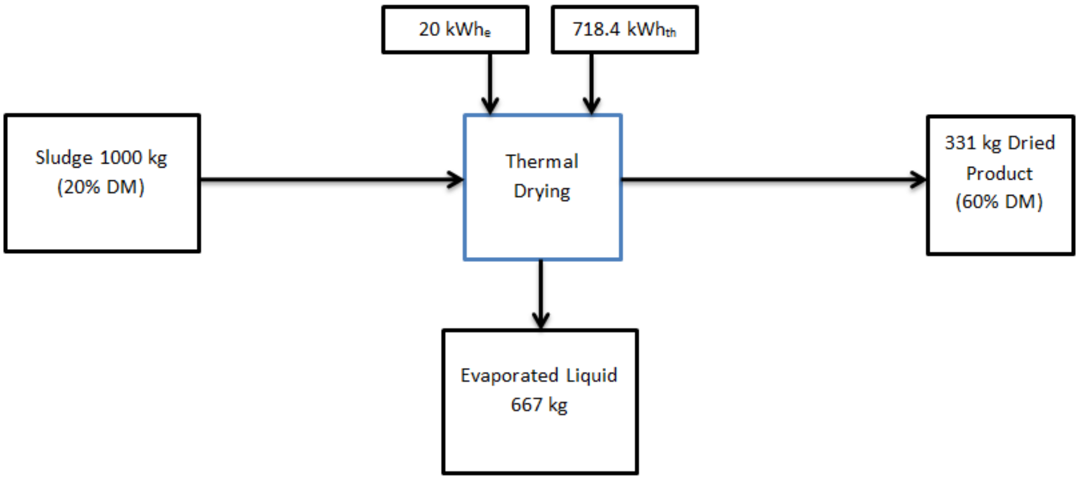


Figure 28: Scenario 2 (PPS)

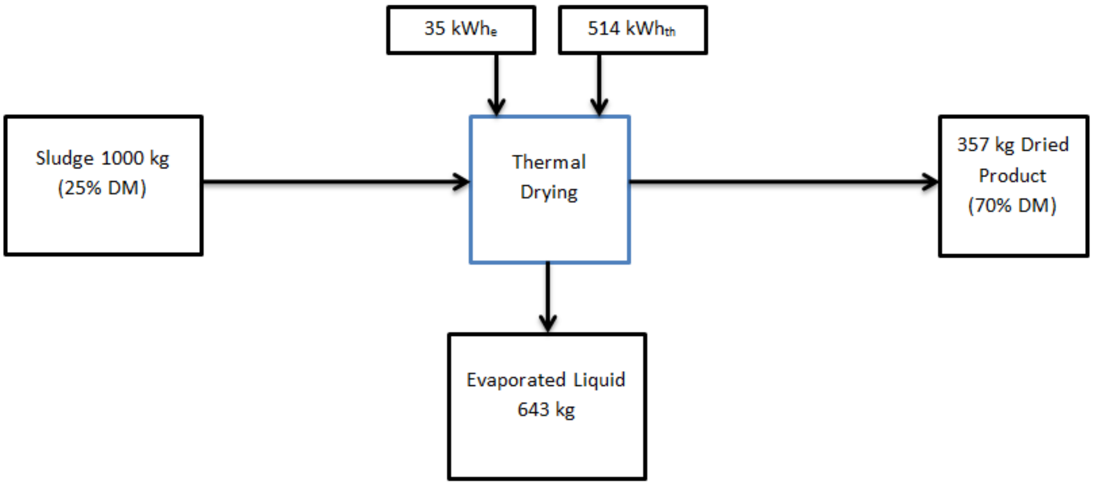


Figure 29: Scenario 2 (ADS)

4.1.3 Scenario 3

Mass and energy flows for the HTC processes follow one of two separate models, as shown in Figures 30 and 31. As stated previously, each model differs in such significant ways as to make comparison between the qualities of the technologies meaningless. For a valid comparison of technologies, standardized feedstock materials and operating conditions would be needed. The models chosen are based on the latest information available, provided by the manufacturers of the technologies. Data provided is in line with reported experimental results (Areeprasert *et al*., 2014; Escala *et al*., 2012). For PPS, a so-called SunCoal model for mass and energy flows was devised based on information provided from SunCoal Industries (SunCoal Industries, n.d.; Wittmann, 2014). It is based on 50 000 tons annually of PPS with 20%DM undergoing HTC in a continuous reactor and a dewatered product with 60%DM. For ADS, a so-called AVA-CO2 model was devised for mass and energy flows based on information provided by AVA-CO2 (AVA CO2 Schweiz AG, 2014; Kläusli, 2014). It is also based on 50 000 tons annually of ADS but with 25%DM, undergoing HTC in a batch reactor and a dewatered product with 70%DM. Key operating parameters are found in Tables 6 and 7 for both models. Both steam and electricity are assumed to be supplied externally. This point will be re-examined in later sections.

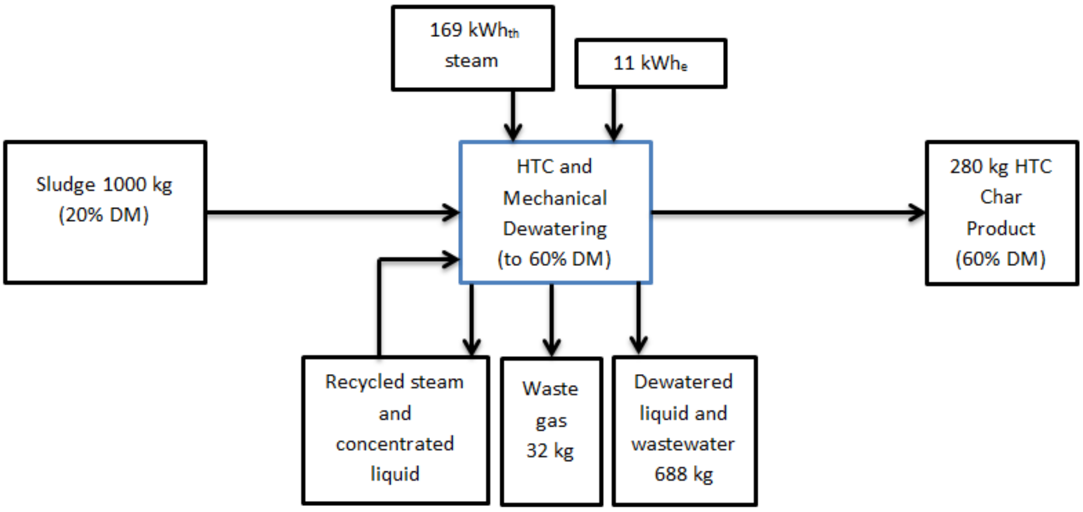


Figure 30: Scenario 3 (PPS)

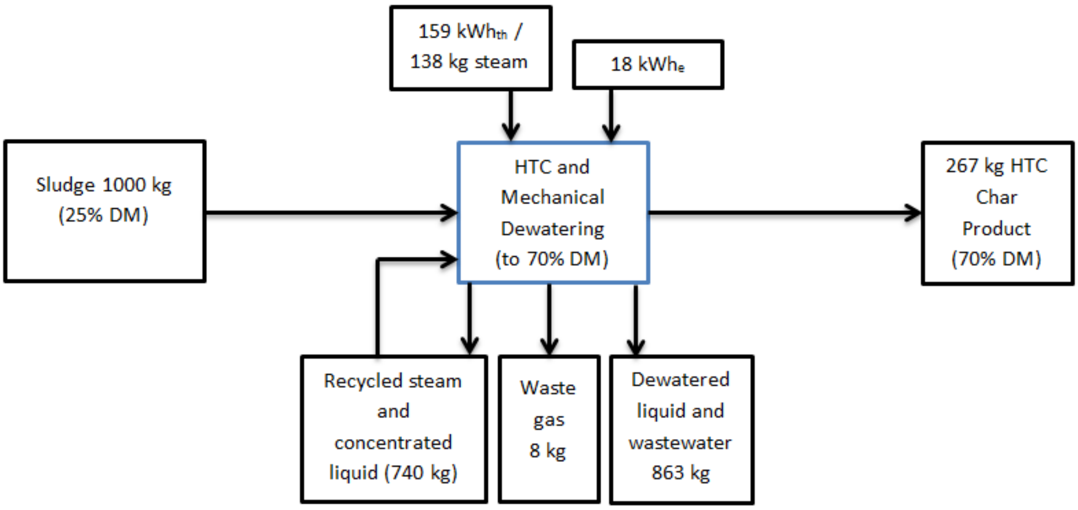


Figure 31: Scenario 3 (ADS)

4.1.4 Scenario 4

Mass and energy flows for Scenario 4 procede in the same fashion as Scenario 3 with noted additions of thermal drying and pelletization. Mass flows related to thermal drying have been extrapolated based on a desired 90%DM end product in both cases. Energy requirements for thermal drying have been extrapolated based on experimental data related to ADS HTC char (Krebs *et al.*, 2013). Thermal energy requirements for drying HTC char are 1.7 MJ per kg of water removed and electrical requirements are 0.066 kWh per kg of water removed. It is assumed that the same energy requirements are applicable for PPS HTC char.

Pelletization is assumed to proceed with no losses and no use of fixatives in a pellet production line capable of handling 1.5 tons per hour. Energy requirements are based on the Zhengzhou Amisy Wood Pellet Production Line (excluding drying system) with a rated capacity of 236 kW. Energy requirements are based on processing 1.5 tons of HTC char per hour or 157 kWh per ton of HTC char processed. Processes are shown in Figures 32 and 33.

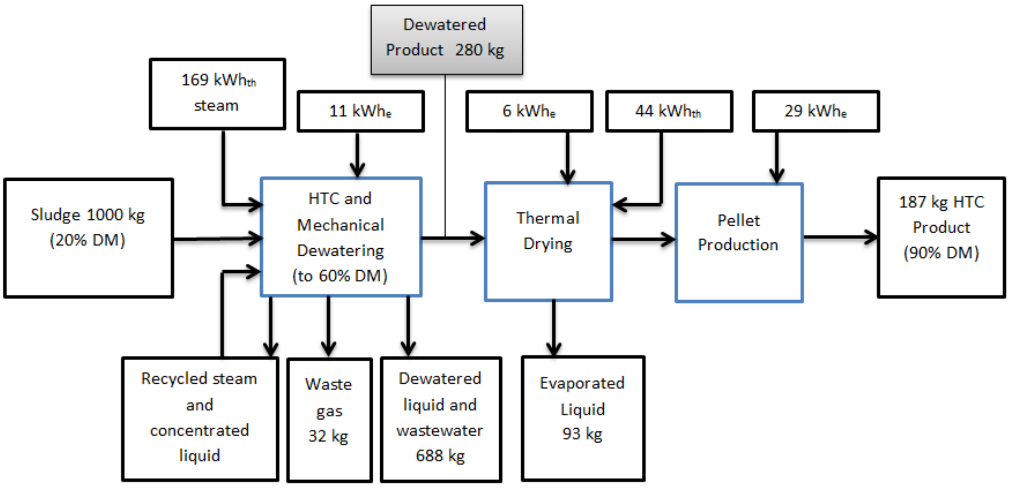


Figure 32: Scenario 4 (PPS)

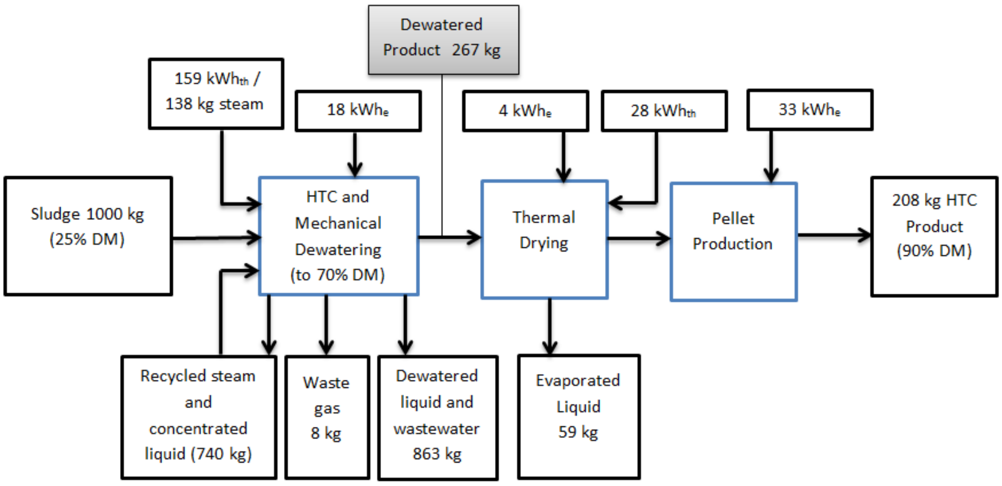


Figure 33: Scenario 4 (ADS)

5 COST FUNCTIONS

Due to the proprietary nature of businesses and technologies involved in this investigation, costs related to many aspects of the models introduced are based on estimates. Efforts were made to ensure that estimates made were reasonable according to the literature or industry representatives. Caution was often advised when dealing with almost all cost functions involved. Each parameter can differ over time as well as geographically. Costs are different in rural and urban environments in some cases. Some prices, such as the important price of HTC char is based on an ability to pay for a completely different commodity (coal), which is itself quite variable, and then adjusted, as the market for HTC char materials is still in its infancy and no reliable price currently exists. In addition, for both ADS and PPS treatment, estimates are based on processing 50 000 tons of raw sludge annually. It is generally agreed that this represents a critical level of capacity, below which the HTC of sludge materials would not be feasible. It is hoped that the economic estimates that follow can provide a well-founded yet conservative benchmark to which more accurate local cost functions can be compared. The effects of variability in costs will be discussed as opportunities and challenges in Sections 6-8.

Estimates for both HTC plant models include the cost of a mechanical press and assume that the location has access to appropriate process steam so that steam generating equipment will not be purchased. The total price of an HTC plant is based on a myriad of customer needs and could be higher or lower by significant levels based on local conditions. Total costs of treatment per ton of raw sludge and key assumptions in calculating treatment costs are found in Tables 16-19. All monetary values are shown in Euros.

Investment estimates are introduced in the Appendix.

Table 16: Total costs of PPS sludge treatment

Factor (€ / ton of raw sludge)	Transport	Gate or treatment fees	Effluent Treatment	Investment (HTC)	Operations and Maintenance (HTC)	Investment (Thermal dryer)	Operations and Maintenance (Thermal dryer)	Investment (Pellet line)	Operations and Maintenance (Pellet line)	Procurement of resources		Energy from fuel	**Total**
										Steam	Electricity		
Scenario 1 - low estimate	0.00	30.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**-30.00**
Scenario 1 -Incineration	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-32.52	**-32.52**
Scenario 2	0.00	0.00	1.00	0.00	0.00	3.35	2.00	0.00	0.00	35.92	2.00	7.71	**-36.56**
Scenario 3	0.00	0.00	1.03	5.03	3.00	0.00	0.00	0.00	0.00	8.44	1.14	6.25	**-12.39**
Scenario 4	2.60	0.00	1.17	5.03	3.00	3.35	2.00	0.17	0.10	10.63	6.17	19.02	**-15.18**

Table 17: Total costs of ADS sludge treatment

Factor (€ / ton of raw sludge)	Transport	Gate or treatment fees	Effluent Treatment	Investment (HTC)	Operations and Maintenance (HTC)	Investment (Thermal dryer)	Operations and Maintenance (Thermal dryer)	Investment (Pellet line)	Operations and Maintenance (Pellet line)	Procurement of resources		Energy from fuel	**Total**
										Steam	Electricity		
Scenario 1 - low estimate	0.00	30.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**-30.00**
Scenario 1 -Incineration	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-48.54	**-48.54**
Scenario 2	0.00	0.00	0.96	0.00	0.00	3.35	2.00	0.00	0.00	25.72	3.47	-2.17	**-37.68**
Scenario 3	0.00	0.00	1.29	11.73	7.00	0.00	0.00	0.00	0.00	7.95	1.80	-2.41	**-32.18**
Scenario 4	2.34	0.00	1.38	11.73	7.00	3.35	2.00	0.17	0.10	9.34	7.10	12.05	**-32.46**

Table 18: Key assumptions in calculations of PPS sludge treatment costs

Key assumptions		
Cost of HTC plant	3000000	€
Cost of Thermal dryer	2000000	€
Cost of pellet production line	100000	€
Interest rate	3 %	
Years of operation	15	
Annual capacity	50000	tons
Operations and maintenance	5 %	
Effluent treatment cost	1,5	€/ton
Electricity cost	0.1	€/kWh
Steam cost	0.05	€/kWh
HTC Char Drying thermal power	0.47	kWh per kg H_2O removed
HTC Char Drying electric power	0.066	kWh per kg H_2O removed
PPS Drying thermal power	718.4	kWh/t of raw sludge
PPS Drying electric power	20	kWh/t of raw sludge
HTC steam power	168.8	kWh/t of raw sludge
HTC electric power	11.4	kWh/t of raw sludge
Pellet production line electric power	236	kWh/t of HTC char

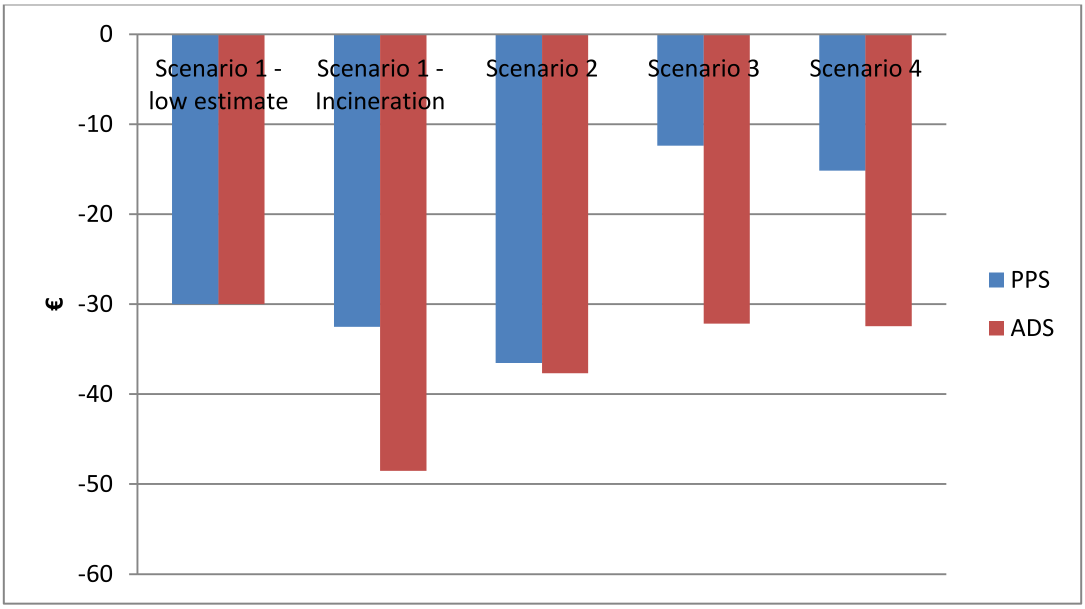
Table 19: Key assumptions in calculations for ADS sludge treatment costs

Key assumptions		
Cost of HTC plant	7000000	€
Cost of Thermal dryer	2000000	€
Cost of pellet production line	100000	€
Interest rate	3 %	
Years of operation	15	
Annual capacity	50000	tons
Operations and maintenance	5 %	
Effluent treatment cost	1.5	€/ton
Electricity cost	0.10	€/kWh
Steam cost	0.05	€/kWh
HTC Char Drying thermal power	0.47	kWh per kg H_2O removed
HTC Char Drying electric power	0.066	kWh per kg H_2O removed
ADS Drying thermal power	0.8	kWh per kg H_2O removed
ADS Drying electric power	0.054	kWh per kg H_2O removed
HTC steam power	159	kWh/t of raw sludge
HTC electric power	18	kWh/t of raw sludge
Pellet production line electric power	236	kWh/t of HTC char

Total costs of sludge treatment are shown in Figure 34. As can be seen, scenarios involving HTC treatment of sludge fall below traditional incineration costs leading to the appearance of HTC as an economically feasible treatment option. In the case of PPS, while treatment still results in a net cost, HTC can offer significant savings over treatments involving traditional drying and incineration. A savings of EUR 20 per ton of sludge could represent annual savings of EUR 1 million annually based on 50 000 tons of sludge.

An interesting observation can be made when comparing direct incineration of sludge to drying and then incinerating. While data for PPS confirm general views that the energy required to dry sludge material cannot be feasibly recovered, data for ADS suggest the opposite – it may be economically feasible to utilize thermal drying before incineration in some circumstances. Upon closer examination, the starting point of raw ADS (25%DM) is a relatively unlikely situation without the extended use of electrical power and operation of a mechanical press. The effort and cost related to dewatering PPS can be assumed to be markedly less. These costs were not considered within the system boundaries of this study.

Figure 34: Total costs of sludge treatment



There are a number of issues related to HTC that have no direct economic cost, but clearly have relevance to this investigation. In addition, due to the number of general assumptions made in this analysis, an examination of some of the ways the HTC process can be integrated into existing infrastructure in order to achieve savings is necessary. The following sections will examine further opportunities and challenges related to HTC from social, environmental and economic perspectives.

6 SOCIAL IMPACTS

6.1 Opportunities

There are several opportunities that can be associated with utilizing HTC technology to process sludge materials. In general, production of HTC char can increase energy security in regions where coal is imported. As demand for coal increases globally, production at a local or regional level will become more attractive. This local or regional initiative will also support more local policy implementation and economic development. HTC char processing will involve local resources and value addition and can lead to increasingly diversified local employment. This boost in employment could help to offset jobs that are currently being lost in the wood processing and pulp and paper industries (Wang *et al*., 2014). The development of a bio-coal industry in general can help promote rural development and entrepreneurship through the creation of new production and distribution systems *(ibid*.). There is also an opportunity to develop local partnerships with smaller-scale combined heat and power (CHP) facilities that will be discussed in Section 8.1.

In terms of specific opportunities to the system introduced in this investigation, utilizing these waste materials as feedstock has many advantages. First, there is little or no competition for these feedstock materials nor do they require the use of land to create energy. All too often, bioenergy feedstock requires the use of land to create a fuel, such as plant material. This land use can sometimes be in competition with food production. Utilizing waste materials as fuel is an important factor in reducing the need for land use change. Second, utilizing sludge materials will help achieve the social goal of reducing the amount of material going to landfills and can help governments achieve carbon reduction targets. While these aspects will be discussed further in Section 7, these goals are not just environmental in nature. They have clearly become goals that satisfy a fundamental social need as well. Lastly, HTC plants are relatively compact and need not demand vast spatial resources. Facilities can be integrated within existing industrial or municipal sludge handling operations with relative ease or stand-alone facilities can be constructed on a relatively small scale. A stand-alone AVA-CO2 plant demands approximately 1 500 m^2 of space (AVA CO2 Schweiz AG, 2014) and a SunCoal plant demands approximately 5 000 m^2 (SunCoal Industries, n.d.) when input capacity is 50 000 tons of sludge per year.

6.2 Challenges

There are also several challenges associated with HTC within the social sphere. Foremost among these challenges is that HTC is a relatively unknown technology. Therefore, pessimism and fear of the unknown may be a barrier to social acceptance. Outside of the charcoal industry, knowledge of so-called bio-coal products is limited. In some countries such as Finland, the HTC char market is currently non-existent. Overcoming this barrier will require some effort. Additionally, utilizing a new method of treating waste materials such as ADS will require public information and education. Human waste materials are a sensitive subject to begin with. It could be an incredible hurdle to get people to change the way they are treated. Further resistance may come to the construction of HTC facilities that process ADS. Fear and suspicion may prevent acceptance of construction plans. There are two positive aspects to this problem though. First, using the term bio-coal may encourage some level of acceptance as this is a term that is already well-used globally. Second, information about HTC and HTC char would be relatively quick and easy to distribute as a growing body of research is currently accumulating.

Local production of HTC char, especially in a facility producing approximately 10 000 tons per year, would result in the need of transport that may find social resistance. The economic models proposed would utilize at least one large lorry shipment out of the HTC plant per day. Using lower capacity lorries would increase traffic and noise further. Therefore, HTC facilities may not be suitably located in residential areas. Next, HTC facilities will be comprised of elements that experience high temperatures and pressures, making worker health and safety an issue that needs to be addressed through appropriate training programs and use of protective clothing. Lastly, in the case of utilizing sludge materials as feedstock, other uses for these materials could be reduced, such as compost or soil remediation production. An argument could be made that reduction in this kind of production could necessitate the increased need to utilize industrial fertilizers or other soil additives. At the same time, it is unlikely that levels of HTC production will significantly affect compost production or soil remediation. In fact, given a limited need of soil remediation, competition for these projects may increase. There is also a possibility of using HTC char as a soil additive instead of as a fuel. A shortage of compost or soil remediation materials seems unlikely on a large scale. However, the local effects of changes in sludge end use should be examined as part of the planning process of an HTC plant.

7 ENVIRONMENTAL IMPACTS

7.1 Opportunities

The use of HTC char as a fuel substitute for coal in a co-combustion scenario would offer the possibility to reduce a number of important emissions. As the HTC coal from these waste feedstock materials could be considered as coming from a biogenic source, greenhouse gas emissions would likewise be biogenic and offer the possibility to lower CO_2 emissions. In addition, for sludge producers that currently landfill sludge materials, HTC treatment not only results in less need for landfilling, but also results in fewer problems with leachate effluents at landfills. As sludge materials have such high moisture content, problems with leachate management could be reduced considerably. The most obvious of these is odour reduction as sludge leachates are often the cause of malodour at landfills. Next, it has already been described how HTC char can be used for several other purposes with environmental benefits in Sections 2.6.

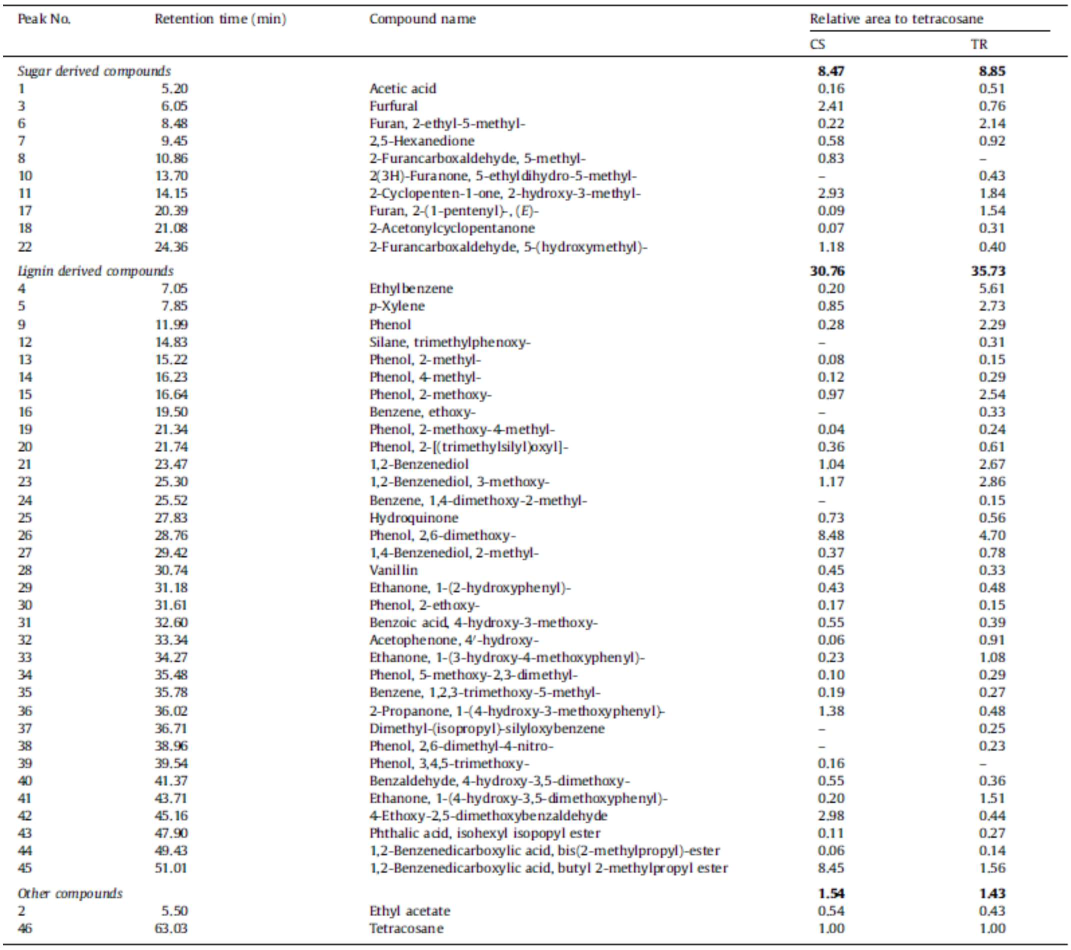
One of the major issues related to the use of these feedstock materials is ash handling and disposal. This issue does not disappear upon HTC treatment, but there is no reason to conclude that recent advances in ash treatment cannot be applied to the ash residues of HTC char. One opportunity to explore is the so-called ASH DEC process. This process has been postulated as a method to reduce high levels of heavy metals in sludge ash while maintaining high levels of phosphorous (Havukainen *et al*., 2012). This results in sludge ash being suitable for use as an agricultural fertilizer. Maintaining P levels in soil has become an increasingly important environmental issue. In addition, less ash from the combustion of the HTC char materials in this study would need to be landfilled. This could obviously offer some economic opportunity as many key assumptions made in this report have been based on rather high costs associated with ash disposal.

Perhaps the greatest opportunities associated with HTC treatment come from the possibility of valuable material recovery from the gaseous and liquid products of the process. As reported in Section 2.5.1, gaseous products are generally less than 10% of the final product of the HTC process and this yield decreases with condition temperatures. As the conditions in the models presented represent rather low temperatures in the range of possible HTC conditions, it is no surprise that gas yields are rather low. For PPS the gas yield was 3.2% and for ADS the yield was 0.8%. This represents annual gas emissions of 1600 tons and 400 tons respectively. The vast majority of this, at least 90%, is CO_2. Up to 4% may be a collection of hydrocarbon gases and the balance would be a relatively even split of H_2 and CO. To date there have been no investigations into the collection, separation or usage of the gaseous products. Therefore, the opportunities of utilizing combustible off-gases are unknown and require further investigation. Collection of a fairly pure form of CO_2 that requires little cleaning may also be an opportunity as carbon capture and storage opportunities develop over time.

Liquid products of the HTC process represent a relatively greater potential for valuable material recovery. Although both of the models presented show a recycling of liquid product throughout the process, the final liquid effluent was somewhat rich in both inorganic and organic compounds of interest. Process liquids from HTC represent a good opportunity for both nitrogen and phosphorous recovery as these elements are found in higher concentration in the liquid product than in the solid product. Currently, AVA-CO2 is investigating the possibilities of P recovery as an integral part of HTC processing of ADS and a phosphorous-free HTC char may be possible (Kläusli, 2014; Krebs *et al*., 2013). It may be possible that a significant portion of HTC process liquids can be used as an agricultural fertilizer. A current impediment to this usage is the somewhat high acidity of process liquids and their high heavy metal content although solutions to this problem are under investigation (Krebs *et al*., 2013). A final opportunity associated with material recovery involves the use of process liquids as a medium for cultivating microalga *Chlorella vulgaris*. A recent study showed that Chemical Oxygen Demand (COD), total nitrogen and total phosphorus can be reduced in HTC process liquids by *C. vulgaris* (Du *et al*., 2012). This not only helps clean process wastewater, but also results in algae with high levels of carbon, hydrogen and lipids. These could then enhance the economic feasibility of an algal biofuel process if such a possibility existed nearby.

The acidity of HTC liquid products may also be a potential area of opportunity. There are several acids of potential commercial interest that are present in significantly high concentrations as to offer the possibility of recovery. Xiao *et al*. (2012) offer an extensive list of compounds found in the liquid product of the HTC process (Table 20). They also suggest that many of these sugar and lignin derived compounds may represent desirable feedstock materials for biodiesel or chemical production. However, there is currently no detailed information in the literature concerning the liquid products of the feedstock materials used in this study. At present, industrial-scale facilities return process liquids to the start of the wastewater treatment process.

Table 20: Major components of the liquid product of HTC (Xiao *et al.*, 2012)



Peak No.	Retention time (min)	Compound name	Relative area to tetracosane	
			CS	TR
Sugar derived compounds			**8.47**	**8.85**
1	5.20	Acetic acid	0.16	0.51
3	6.05	Furfural	2.41	0.76
6	8.48	Furan, 2-ethyl-5-methyl-	0.22	2.14
7	9.45	2,5-Hexanedione	0.58	0.92
8	10.86	2-Furancarboxaldehyde, 5-methyl-	0.83	–
10	13.70	2(3H)-Furanone, 5-ethyldihydro-5-methyl-	–	0.43
11	14.15	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	2.93	1.84
17	20.39	Furan, 2-(1-pentenyl)-, (*E*)-	0.09	1.54
18	21.08	2-Acetonylcyclopentanone	0.07	0.31
22	24.36	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	1.18	0.40
Lignin derived compounds			**30.76**	**35.73**
4	7.05	Ethylbenzene	0.20	5.61
5	7.85	*p*-Xylene	0.85	2.73
9	11.99	Phenol	0.28	2.29
12	14.83	Silane, trimethylphenoxy-	–	0.31
13	15.22	Phenol, 2-methyl-	0.08	0.15
14	16.23	Phenol, 4-methyl-	0.12	0.29
15	16.64	Phenol, 2-methoxy-	0.97	2.54
16	19.50	Benzene, ethoxy-	–	0.33
19	21.34	Phenol, 2-methoxy-4-methyl-	0.04	0.24
20	21.74	Phenol, 2-[(trimethylsilyl)oxyl]-	0.36	0.61
21	23.47	1,2-Benzenediol	1.04	2.67
23	25.30	1,2-Benzenediol, 3-methoxy-	1.17	2.86
24	25.52	Benzene, 1,4-dimethoxy-2-methyl-	–	0.15
25	27.83	Hydroquinone	0.73	0.56
26	28.76	Phenol, 2,6-dimethoxy-	8.48	4.70
27	29.42	1,4-Benzenediol, 2-methyl-	0.37	0.78
28	30.74	Vanillin	0.45	0.33
29	31.18	Ethanone, 1-(2-hydroxyphenyl)-	0.43	0.48
30	31.61	Phenol, 2-ethoxy-	0.17	0.15
31	32.60	Benzoic acid, 4-hydroxy-3-methoxy-	0.55	0.39
32	33.34	Acetophenone, 4′-hydroxy-	0.06	0.91
33	34.27	Ethanone, 1-(3-hydroxy-4-methoxyphenyl)-	0.23	1.08
34	35.48	Phenol, 5-methoxy-2,3-dimethyl-	0.10	0.29
35	35.78	Benzene, 1,2,3-trimethoxy-5-methyl-	0.19	0.27
36	36.02	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	1.38	0.48
37	36.71	Dimethyl-(isopropyl)-silyloxybenzene	–	0.25
38	38.96	Phenol, 2,6-dimethyl-4-nitro-	–	0.23
39	39.54	Phenol, 3,4,5-trimethoxy-	0.16	–
40	41.37	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	0.55	0.36
41	43.71	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.20	1.51
42	45.16	4-Ethoxy-2,5-dimethoxybenzaldehyde	2.98	0.44
43	47.90	Phthalic acid, isohexyl isopopyl ester	0.11	0.27
44	49.43	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl)-ester	0.06	0.14
45	51.01	1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester	8.45	1.56
Other compounds			**1.54**	**1.43**
2	5.50	Ethyl acetate	0.54	0.43
46	63.03	Tetracosane	1.00	1.00

Anaerobic conditioning of HTC process liquids offers significant potential for energy recovery from produced biogas (Reza *et al*., 2014). Reza *et al*. (2014) report that several studies have demonstrated that biogas produced from the anaerobic treatment of HTC liquid products can yield methane in sufficient quantities to produce a more favourable energy balance. Mesophilic batch digestion tests showed that methane production can reach levels of 0.65L/g $_{TOC}$ and that up to 60% COD can be removed within 8 days (Wirth *et al*., 2012). Wirth *et al*. (2012) modelled the use of produced gas within an HTC plant designed to use natural gas as a heat source for steam production and found that produced methane may contribute to economic viability. It is unclear whether such gases can be collected and sold as a valuable product although this remains an interesting area of opportunity.

7.2 Challenges

Despite the fact that hydrothermal carbonization has attracted a great deal of research attention over the past decade, there are still a large number of unknowns related to the nature of HTC products when they are produced on an industrial scale. In particular, many assumptions are made about the liquid and gaseous effluents from the process that are based on laboratory or pilot scale projects or that have been generally applied from results concerning one feedstock to another. It remains somewhat open whether many of these assumptions will hold true over the long term. Therefore caution must be exercised.

Detailed studies have not been completed for the feedstock materials in question related to either gaseous or liquid emissions. No studies currently exist that detail the gaseous emissions over time of the feedstock materials in question. Particularly worrisome are the unknown quantities of hydrocarbon trace gases being released into the environment as some greenhouse gases have much higher global warming potential than others. More accurate measurement and reporting are needed.

Regarding liquid products of HTC, it has been widely reported that both aerobic and anaerobic treatment of effluents are effective (Funke & Ziegler, 2010; Ramke *et al*., 2009). However, it has also been reported that the liquid product contains higher amounts of some elements, such as chlorine and heavy metals, relative to the solid product. As these elements are currently introduced back to the beginning of the wastewater treatment process, it is unclear what long-term effect this will have on the nature of the sludge feedstock. If, over time, these elements accumulated in the sludge feedstock, then it may be possible for higher concentrations to eventually be found in the HTC char, possibly negating any current benefit. Further study of the flow of such compounds is needed for a wide range of feedstock materials, particularly sludge materials (Ramke *et al*., 2009).

8 ECONOMIC IMPACTS

8.1 Opportunities

8.1.1 Integration with existing facilities and services

In developing the HTC models presented in this analysis, key assumptions were derived from the perspective of an HTC facility operating somewhat independently from the wastewater facilities that supplied the sludge materials and the surrounding industry that supplied the wastewater or incinerated the sludge or HTC char. Of course, higher degrees of integration of these facilities could allow for increased process efficiencies and cost savings. Primarily, using steam and electricity generated within a closed industrial system would reduce acquisition costs significantly. One key assumption was that steam and electricity were provided from an external source and costs reflected retail values of these resources (EUR 0.05 kWh_{th} and EUR 0.1/ kWh_{e}). However, the costs of internally produced energy could be as low as EUR 0.04/ kWh_{th} and EUR 0.07/ kWh_{e} at a pulp and paper plant with its own energy production plant. This would reduce the total costs of sludge treatment in Scenarios 2-4 for PPS to EUR 28.78, 10.36 and 11.21 respectively. For ADS, costs would drop only moderately to EUR 31.49, 30.05 and 28.46 respectively. Another key assumption was that the treatment of effluent liquids from the HTC process was performed externally and the cost reflected a market price of treatment. By reducing effluent amounts by valuable material recovery or finding other uses for the effluent (such as use as a liquid fertilizer after heavy metal removal) as well as using an internal price of effluent treatment, further savings are possible in Scenarios 2-4, perhaps up to EUR 0.75 per ton of raw sludge for both PPS and ADS. Lastly, key assumptions were made concerning the price of the HTC plant, which vary dramatically based on the level of integration with existing facilities and services. Further savings on plant price are possible as a result of higher levels of integration.

8.1.2 Integration with other facilities and services

The integration of HTC plants with other related activities also offers potential opportunities in the future. In one case, a modelled integration of an HTC plant with a CHP facility showed an ability to produce biocoal pellets from waste materials with improved efficiency (Erlach *et al*., 2011). At the same time, the author cautioned that further study was still needed before conclusions could be reached concerning industrial-scale production.

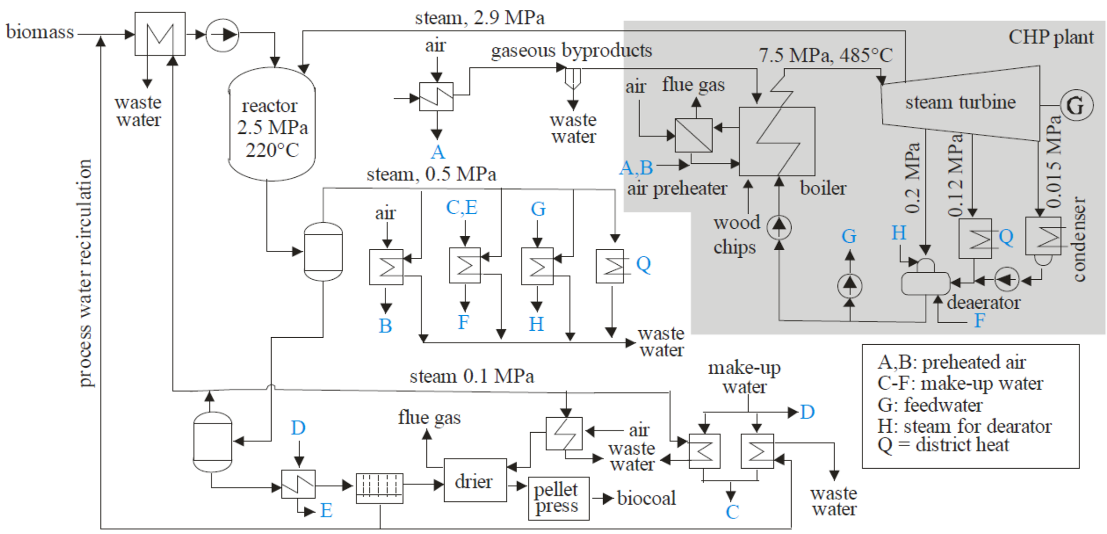


Figure 35: Flow diagram from an integrated HTC and CHP plant (*ibid.*)

In addition, a recent study suggests that integrating the efforts of HTC and torrefaction plants could result in mutual benefit (Reza *et al.*, 2014). The authors concluded that by mixing 90% torrefied char and 10% HTC char into a bio-coal pellet, a more durable pellet with higher energy density could be achieved without the use of binding agents during pelletization. Further, it seems likely that savings could be achieved by through possible use of common process energy (steam and electricity) or equipment (dryers, presses, etc.).

8.1.3 Developing a bio-coal market

Currently in Finland, a market for bio-coal products does not exist. While this will be discussed as a subsequent challenge, new opportunities for production have vast potential. In Finland, the potential to replace coal with biomass fuels will be about 7-8 TWh annually (Wang *et al.*, 2014) and a bio-coal market is currently developing with torrefied wood products leading the way. Demand will not only come from large, centralized coal-burning facilities, but is expected to also come from district heating and CHP plants throughout the country as well as from small-scale central housing heating systems. So-called “early birds” in the bio-coal market may therefore experience very little competition in this new market for some time to come. Upon further market development, economies of scale will be established in addition to improved infrastructure and distribution systems (*ibid.*).

The forestry sector seems to be in a particularly good position to act as the vanguard of the Finnish bio-coal revolution due to its well-established chains of supply and distribution systems.

Current global bio-coal markets are inevitably linked to the market for coal itself. The price of coal as well as the price of carbon reduction credits will ultimately affect the market's ability to pay for bio-coal, as outlined in Section 3.3.4. At present, both the price of coal and carbon reduction credits are at fairly low levels. Improvements in these areas could result in potential windfall profits for bio-coal producers. In addition, government regulation or support programs could have a positive effect on the Finnish domestic bio-coal market. Currently, no such regulation or support exists but national and EU policy framework exists to recognize how a maturing bio-coal industry can support government commitments to sustainability and the development of a bio-economy. It seems unlikely that the bio-coal market will remain unsupported.

8.1.4 Developing local partners

A major opportunity for HTC processing of sludge materials involves the enhancement and diversification of local and regional economic development (Wang *et al.*, 2014). Some of the benefits of bio-coal production have already been stated in Section 6.1. However, there are many more opportunities to develop chains of small- and medium-sized scale entrepreneurs including transporters and distributers as well as local governments and energy producers. In some cases this co-operation will be an essential element of success. In areas outside the capital region of Finland, individual sludge producers (either municipal or industrial) may not have the required amount of sludge to achieve a minimum viable capacity of approximately 50 000 tons of sludge annually. Therefore, co-operation with other sludge producers will be important. Alternatively, this could mean an opportunity for an independent waste management company to receive these waste streams from a number of sources in exchange for an appropriate reception fee. These reception fees could be similar to those already suggested as treatment fees for sludge, or EUR 30-80 per ton of wet sludge. In the Lappeenranta to Simpele corridor of the South Karelia region of Finland, there are four major pulp / paper plants that produce approximately 3 million tons of pulp per year. This could result in more than 100,000 tons of mixed pulp and paper sludge per year and so offer an attractive economy of scale for HTC operations. The distance between these plants is approximately 80 km. Locating an HTC plant near the midway point of this corridor, in Imatra where the largest of the pulp and paper mills is located, could be an optimal solution. The HTC char product could be returned to those same companies as a fuel, sold to one of many local heat or CHP plants, or delivered to a planned torrefaction plant located roughly 100km to the north of Lappeenranta in the municipality of Ristiina. Ground transport between facilities can be efficiently accomplished by road or rail. Three of the four mills are also linked by a well-used waterway. The companies included each have well-developed logistical know-how and regional transport companies are available to handle large quantities of freight due to the significant presence of the forest industry. Opportunities for further research and development could be supported by partnerships with Lappeenranta University of Technology.

8.1.5 Other opportunities

As discussed in Sections 3.2.1 and 3.2.2, the production of sludge materials is a complex process for both PPS and ADS. In addition, there are two major types of sludge that are usually mixed – primary and secondary. An opportunity therefore exists to investigate the possibilities related to removing some or all of the sludge streams from an earlier stage of production or to include only part of the sludge materials in the hopes of making the best fuel possible from HTC treatment. For instance, further study is needed to determine the feasibility of using ADS materials in HTC treatment prior to the final stage of anaerobic digestion. One study suggests that non-stabilized sewage sludge could result in a more favourable fuel after HTC than ADS (Escala *et al*., 2012). The HTC char from the non-stabilized sewage sludge had a higher carbon content as well as lower H/C and O/C ratios. In addition, levels of nitrogen and sulfur were lower and higher heating values were higher. For PPS, there may be an opportunity to produce a higher quality HTC char fuel from primary sludge than either secondary sludge or a mixed sludge. In particular, primary sludge generally contains much lower levels of ash than secondary sludge, something that ultimately affects the quality of the HTC char fuel. Further study is needed on the quality of HTC char from primary PPS and whether sufficient quantities of primary PPS exist in a given context to create an appropriate economy of scale for industrial HTC treatment.

A final opportunity exists in determining the feasibility of mixing more than one biomass or waste feedstock prior to HTC. In many cases sludge materials are mixed with bark or forest residues prior to incineration. This begs the question of whether it would be feasible to mix such feedstock materials with PPS or ADS prior to HTC. Although data has not been published, SunCoal reports that such mixing works well and may help to solve a number of problems (Wittmann, 2014). With some pre-treatment, such as grinding, and mixing according to a prescribed recipe, a compound can be created that has lower overall moisture and ash contents. The lower moisture content can mean that higher amounts of recycled process liquid can be utilized for greater energy savings. Lower ash content should also be found in the HTC char, resulting in a higher quality fuel. Adding another biomass or waste stream will also help achieve a greater HTC plant capacity and allow for an improved economy of scale. For pulp and paper companies, bark and other forest residues may not even represent an additional expense. For municipalities, other biomass streams may also be available in abundance such as household green waste or agricultural residues. For each, establishing suitable supply and a standard mixing ratio would be essential. Research involving large-scale testing of HTC of mixed waste streams offers great potential as the literature has been dominated by descriptions of HTC of single feedstock materials.

8.2 Challenges

While the Finnish bio-coal market could be viewed with optimism, one could equally be pessimistic. The fact that a current market does not exist is an obstacle that requires significant investment and effort to overcome. Importantly, the price of bio-coal in Finland has yet to be firmly established. While an attractive ability to pay for bio-coal products exists, end users may negotiate prices well below their ability to pay. Economic feasibility of HTC char sales would be dependent on establishing long-term price guarantees with end-users, primarily large-scale coal burning facilities, which may be difficult to implement. Currently, co-firing with bio-coal (from torrefaction) at an industrial level is being studied in Finland and the results of these studies may determine future industrial-scale feasibility of HTC. In addition, bio-coal will need to compete with other forms of biomass for its share in the biofuel market. Therefore, prices for bio-coal will depend not only on the price of coal, but on the prices of many other biomass fuels as end users weigh the pros and cons of each.

Another important challenge in developing the use of HTC char is overcoming its obscurity in Finland. While the concept of bio-coal is familiar and attractive worldwide, char from HTC is not. Compounding this problem is the unknown and unproven technology involved in HTC. Wood chips and pellets are known and attractive commodities in Finland that individuals and businesses are beginning to embrace more and more. Awareness of HTC, its products and its feedstock materials will need to increase in order to overcome a natural resistance to something new. It may be particularly difficult to convince individual consumers to burn HTC char from ADS in their homes even when confronted with its many benefits.

Lastly, due to the fact that HTC at an industrial scale is currently in its infancy, there are many technological unknowns over the long term. First, the recirculation of process liquids has been studied from a chemical and efficiency perspective, but the effects of maintaining a high pressure and acidic environment in HTC reactors is unknown over time. The first generation of HTC reactors, both continuous and batch, are currently less than 5 years old. Industrial–scale plants are estimated to have a lifetime of 15 years. The effects of acid corrosion on reactors may lessen that time frame or result in the need of upgrading or repair in order to reach that time frame. Maintenance requirements may also differ from expectations. Secondly, availability of the HTC process or equipment is an area that has not been investigated in the scientific literature. It is therefore unknown what effects disruptions in the flow of feedstock materials might have on HTC plants. Nor is it known how downtime in an HTC plant would affect flows of materials both up and down stream. Storage of feedstock and product materials may be an important aspect of HTC plants. Lastly, large-scale co-combustion with HTC char remains an area of unknown interest in the scientific community. Studies with torrefaction char are currently underway in Finland and around the world, but no studies currently exist that detail the combustion behaviour of HTC char in boilers on an industrial scale or over long periods of time. It remains unknown what effect the combustion of HTC char will have on boilers and heat transfer surfaces due to the high amounts of ash in HTC chars from sludge materials. Ash handling may represent a large obstacle for many end users. In addition, high amounts of particulate matter in flue gases may provide an increased challenge to air pollution control devices. These unknowns may be an obstacle to the sale of HTC char as a fuel.

9 RECOMMENDATIONS AND CONCLUSIONS

Throughout this analysis, a number of estimates and assumptions were made that result in difficulties in making conclusions beyond generalizations. In fact, it would be unwise to reach conclusions regarding the feasibility of HTC treatment for a specific development context without considering how these estimates and assumptions would be different in a specific, real-life situation. In addition, there exist a number of open areas of opportunity and challenge associated with HTC treatment within the spheres of society, environment and economics that may be applicable to some contexts, but not to others. The process of determining ultimate feasibility of a given project should involve consideration of these general observations followed by a detailed analysis of the social, environmental, economic and technological factors involved in such a project. The recommendations that follow represent criteria that must be used to determine the feasibility of a given project.

Feedstock

1. Detailed information about the feedstock must be collected and analysed. An HTC treatment program will generally require a minimum flow of 50 000 tons per year of wet sludge. Higher capacity of the plant can greatly reduce costs. The flow of feedstock must be known on an hourly, daily, weekly and yearly basis. Storage of feedstock may be required to ensure continuous HTC and prevent problems in the event of HTC plant downtime.
2. Information regarding other uses of sludge feedstock should be known in order to determine whether reduction in sludge amounts for these purposes will have a detrimental effect. In many cases HTC can serve as one of many treatment options for sludge. Accurate cost factors for all other treatment options must be known in order to determine relative economic feasibility of HTC. Producers of sludge can develop a variety of treatment strategies based on social, economic and environmental goals.
3. An ultimate and proximate analysis of the intended feedstock or feedstock mixture and its HTC product is mandatory. The major industrial HTC plant manufacturers each offer testing possibilities in pilot or other facilities.

Generally this involves sending samples of approximately 100 kg of feedstock to the manufacturer in order to gain accurate results. Economic feasibility is often included in this analysis. Costs of such testing range from EUR 6 000 to 15 000.

HTC Plant

4. Careful consideration must be made regarding the location of the HTC plant. Spatial requirements should be considered as well as the need for heavy transport equipment throughout the lifetime of the facility. In cases where pellet production is planned, facilities can demand over 5 000 m^2 of floor space. High roof lines and large doors should be planned for buildings that involve transport and storage.
5. Locating HTC treatment close to the source of the feedstock is preferable. In many cases feeding systems have been designed for sludge-based HTC plants that involve pipelines or screw systems from wastewater treatment facilities directly to the HTC plant.
6. Location of the HTC plant close to the end use of the solid product should also be considered. Transport distances between production of the end product and end users should be minimized. When ground transport is necessary, an analysis of shipping frequency and truck size will be necessary.
7. All HTC plants require electricity and steam. Sludge producers may have access to their own resources, which can significantly reduce HTC production costs. In addition, the cost of stand-alone HTC plants will be higher due to the need for steam generation.
8. A careful assessment of needs will be required. HTC plants can be designed for a number of possible scenarios. The HTC reactor is just one component of a complete system that can include feeding systems, steam generation, mechanical presses, thermal dryers, wastewater treatment and pellet production systems. Many of these components can be purchased from other distributers or may already be part of a company’s facilities.
9. HTC plant manufacturers should provide details regarding expected operations and maintenance activities. In some cases, the manufacturers can

provide staff training, remote monitoring services as well as maintenance contracts.

10. Installation and transport costs related to the HTC plant should be included in cost estimates. These costs can vary dramatically from place to place. HTC plant components are generally shipped in standard shipping containers by land or sea.
11. Local authorities should be consulted regarding land use or building permits as well as regarding the need of an environmental impact assessment. The HTC plant manufacturer may offer valuable help in these regards.

Fuel use or sale

12. Determining the end use of the HTC char product will have a great impact on the extent of post-treatment. Incineration of HTC char products is not suitable for all boiler types due to levels of ash and moisture. Intended end-uses must be specified before a detailed feasibility study can be completed.
13. Before the choice of producing an HTC char pellet is made, a careful analysis of the local bio-coal market is necessary. This should include price projections for the HTC char product that reflect local demand.
14. Transport distances and related costs can vary significantly. Local and regional transport companies should be consulted during planning. Bulk transport of pellets in specially designed trucks may be possible, thereby reducing costs.
15. Cooperation with producers of terrified bio-coal pellets should be explored.

It is clear from Figure 34 and the discussion in Section 6-9 that HTC treatment of the waste sludge materials considered in this study is feasible in a general sense. If one starts from the assumption that treating these waste materials will always represent some kind of cost to those that produce them, then the challenge is to find a treatment solution that is not only cost effective, but sustainable. Landfilling as a treatment solution will effectively end in the near future in much of Europe, and HTC can rise as a feasible replacement. In addition, it can be seen as a competitive alternative to traditional sludge incineration scenarios, providing benefits that go beyond economics and suit the social and environmental goals of responsible companies and municipalities.

The case for HTC treatment of PPS seems to be slightly stronger than for ADS. Figure 34 shows that Scenarios 3 and 4 for PPS are well below the lowest treatment alternative estimate while Scenarios 3 and 4 for ADS are just above the EUR 30 estimate. However, the ultimate feasibility of each will be determined by the exact range of alternative treatment options available in a given context. In any event, both scenarios involving HTC for both feedstock materials are favourable to direct incineration or incineration preceded by drying. Therefore, considerable savings can be realized by HTC treatment of both feedstock materials. The choice of which HTC Scenario would be best for a given context would be determined by the possibility for a sludge producer to incinerate their own HTC char and demand for HTC char as fuel in that particular context. For some sludge producers, remoteness may dictate that the HTC char must be incinerated locally. For others, a higher demand for the product and ease of transport may result in high external demand for the solid fuel product. In some cases, high demand for other carbon end products may result in the feasibility of other uses of the HTC char product in whole or part.

The South Karelia region of Finland may offer an attractive environment for HTC treatment of PPS through the collaboration of an existing cluster of pulp and paper mills or by an external waste management company. Necessary elements for sustainable HTC treatment of pulp and paper sludge appear to be in place: abundance of feedstock materials to provide a good economy of scale, availability of technological solution, ability to integrate with existing production facilities, ease of transport, and excellent market potential for bio-coal. Of course, a number of questions remain related to the exact details of the operating environment, but the framework above can provide guidance for how ultimate feasibility can be measured.

The region of South Karelia is by no means unique in this regard. Many places in the world offer similar conditions of feasibility for the utilization of HTC treatment of a wide range of feedstock materials. In many regards, HTC is poised to compete amongst the number of pre-treatment options for biomass and waste that can create new and more diverse solutions for waste management in addition to value-added products. Certainly, there are barriers to overcome. Perhaps the greatest of these is conservatism and fear of the unknown. At the same time, concerns about energy security and climate change have excited a spirit of experimentation, innovation and motivation to look beyond traditional carbon-based materials towards new frontiers. HTC can offer ‘a gentle way’ of dealing with the so-called carbon problem by offering new possibilities and a range of new carbon-based solutions. The ‘turn’ that was introduced at the beginning of this investigation is possible if solutions are crafted from the essence of the problem itself. A growing body of scientific research and new industrial potential suggests that hydrothermal carbonization can contribute to a more sustainable future.

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APPENDIX

Investment estimates for HTC plant models (SunCoal and AVA-CO2), Thermal dryer and Pellet Production Line.

SunCoal HTC Plant
(Complete delivery by main vendor)
Capacity of 50000 tons per year of raw sludge

Construction Foundations (concrete work)	Included main machinery
Main machinery Crusher and feeding system Washing system HTC reactor tank Flash tank high Flash tank low Piping and valves Pumps Mechanical filter press Product handling and storage Process and waste water treatment Electrification & Automation Erection, transportation complete	2 500 000
Other Electrification	Included main machinery
Piping and valves	Included main machinery
HVAC	Included main machinery
Engineering	100 000
Infrastructure	100 000
Project management	50 000
TOTAL **RESERVE**	**2 750 000** **250 000**
TOTAL INVESTMENT	**3 000 000**

AVA-CO2 HTC Plant
(Complete delivery by main vendor)

Capacity of 50000 tons per year of raw sludge

Construction Foundations (concrete work)	Included main machinery
Main machinery Crusher and feeding system Preheating and mixing tank 6 HTC reactors tanks Flash tank high Flash tank low Piping and valves Pumps Mechanical filter press Product handling and storage Process and waste water treatment Electrification & Automation Erection, transportation	5 900 000
Other Electrification	Included main machinery
Piping and valves	Included main machinery
HVAC	Included main machinery
Engineering	200 000
Infrastructure	200 000
Project management	100 000
TOTAL **RESERVE**	**6 400 000** **600 000**
TOTAL INVESTMENT	**7 000 000**

Thermal dryer
(Complete delivery by main vendor)
Capacity of 3-10 tons per hour

Construction Foundations (concrete work)	Included main machinery
Main machinery Andritz Belt Drying System Belt conveyor, belt dryer, screw conveyor Cyclone, fans, air filter, silencer Electrification & Automation Erection, transportation	1 500 000
Other Electrification	Included main machinery
Piping	Included main machinery
HVAC	Included main machinery
Engineering	100 000
Infrastructure	100 000
Project management	100 000
TOTAL **RESERVE**	**1 800 000** **200 000**
TOTAL INVESTMENT	**2 000 000**

Zhengzhou Amisy Pellet Production Line
(Complete delivery by main vendor)
Capacity of 1.5 tons per hour

Construction	Foundations (concrete work)	Included main machinery
Main machinery		
	Crushing and drying system	16 500
	Magnetic separator, Belt conveyor, Hopper	
	Air fan, Collector	
	Belt conveyor, Feeding auger, Hammer mill	
	Pellet mill & Packaging system	47 700
	Conveying auger, pellet mill, air fan, collectors, air locks	
	Belt conveyor, Cooler with screen, bucket conveyor	
	Final product bin, automatic packaging machine	
	Sewing conveyor	
	Electricity control box	4 200
	Erection, transportation	11 600
	Electrification & Automation	
Other Electrification		Included main machinery
Piping		Included main machinery
HVAC		Included main machinery
Engineering		5 000
Infrastructure		5 000
Project management		5 000
TOTAL		**95 000**
RESERVE		**5 000**
TOTAL INVESTMENT		**100 000**